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RAMAN SPECTRA OF INORGANIC COMPOUNDS RELATED TO SOLID STATE TRIBOCHEMICAL STUDIES

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13. ABSTRACT *(Maximum 200 words)*

The accomplishments of this research program were twofold: a) establish a basic Raman spectral library for materials related to solid-state tribological studies, and b) develop a usable analytical approach for this technology in the Materials Directorate. The research was concerned with the characterization of the Raman spectra and how observed changes in these data may reflect the stress placed on a crystal structure during wear testing. This type of study is very important to further increase the understanding and applications of Raman spectroscopy to the field of tribology.

This report contains a library of 51 Raman spectra obtained in the energy region 100 to 925 cm^{-1}.

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FOREWORD

This technical report was prepared by N. T. McDevitt, Ramspec Research, and J. S. Zabinski, Nonstructural Materials Branch, Nonmetallic Materials Division, Wright Laboratory. The work was initiated under Project 2303Q101, WUD 50 and 51, monitored by Dr. J. S. Zabinski.

This report covers work performed in-house during the period January 1994 to October 1995.

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Section 1.0

Introduction

1.1 History

Obtaining Raman spectra prior to the early 1960s was difficult due to the weakness of the Raman effect and the optics necessary to use the mercury lamp sources and collect the scattered light. Raman spectroscopy became much easier when the highly monochromatic laser source was made available to excite Raman scattering routinely from all sizes of samples. In particular, laser sources facilitate obtaining data from solids, and a number of papers are reported in the literature [Ref. 1-3]. Data on the Raman spectra of minerals have been reported by Griffith [Ref. 4].

1.2. Crystal Structure and the Raman Correlation Method

When electromagnetic radiation interacts with a crystal lattice, a photon may be absorbed provided the wave vector and the energy are conserved. This wave vector is extremely small when compared with the wave vector corresponding to the edge of the Brillouin zone. Since the wave vector of the laser light is much smaller, first-order inelastic light scattering will take place and allow the study of the excitations near the center of the Brillouin zone where the wave vector is essentially zero. This first order Raman scattering allows observations of the vibrations of a crystal called lattice modes. Lattice modes are the motions of the

molecules, within a Bravais cell, relative to one another. Selection rules state that lattice modes will give rise to Raman scattering when a change in one or more components of the polarizability of the crystal occurs during a vibration. The Raman tensor that describes this physical parameter for each mode is governed by the symmetry of the scattering crystal.

Based on a factor-group analysis, the correlation method [Ref. 5] is used to derive the vibrational selection rules for the crystals of interest in this study. The crystal structure of the material dictates the orientation of all groups within the crystal. The crystal lattice will determine the space group, which will contain the site symmetries of the atoms in the unit cell. The crystallographic unit cell may be identical with the Bravais cell or it may be larger by some simple multiple. The Bravais space cell is used by molecular spectroscopists to obtain the irreducible representation for the lattice vibrations. The number of molecules per Bravais unit cell will give us the number of equivalent atoms of each kind that are present. From the space group and the X-ray crystallographic tables the site symmetry of each atom may be determined. The displacements described will become the lattice vibrations in the crystal. Knowing the site species for these displacements, each species of the site group can be related to a species of the factor group. This correlation explicitly identifies the species of the lattice vibration in the crystal and further allows the prediction of the number of Raman and infrared active vibrations.

Crystal structures may have bonding forces ranging from primarily covalent to ionic. In covalent bonding the mass of the atoms will strongly determine the frequency position of the vibration. However, for crystals

containing primarily a lattice-like structure, only the factor group is relevant. It is important to realize that in these crystals the observed frequencies arise primarily from the constraints placed upon the molecules by the unit cell structure.

Table 1 shows the predicted first order optical phonons of some inorganic materials. The NaCl crystal has atoms lying on the same site and shows no first-order Raman activity. The two polymorphs of TiO_2 have atoms lying on different sites and have distinct Raman activity showing the analytical potential of Raman spectroscopy with solids.

TABLE 1

First Order Raman Activity

Structure	Space Group	Factor Group	Site Symmetry	Actvity
NaCl	O^5_h	O_h	Oh;Oh	no Raman
CaF	O^5_h	O_h	Oh;Td	1 R
diamond	O^7_h	O_h	Td	1 R
graphite	D^4_{6h}	D_{6h}	$D_{3h};d_{3h}$	2 R
TiO_2(anatase)	D^{19}_{4h}	D_{4h}	$D_{2d};C_{2v}$	6 R
TiO_2(rutile)	D^{14}_{4h}	D_{4h}	$D_{2h};C_{2v}$	4 R
MoS_2	D^4_{6h}	D_{6h}	$D_{3h};C_{3v}$	4 R
MoO3	D^{16}_{2h}	D_{2h}	C_s	24 R
WS_2	D^4_{6h}	D_{6h}	$D_{3h};C_{3v}$	4 R
WO_3	D^{11}_{2h}	D_{2h}	$C_i;C_2$	18 R
Sb_2O_3	O^7_h	O_h	$C_{3v};C_{2v}$	9 R
ZrO_2	C^5_{2h}	C_{2h}	C_1	18 R

Section 2.0

Instrumentation

The energy source used in this study was a Lexel argon-ion laser (Model 95) set at 514.5 nm that delivered between 50 and 150 mW of power, depending upon the sample studied. The scattered radiation was not analyzed and was directed into a Spex 1877E triplemate monochromator. The Raman data were collected by a 1024 element intensified silicon photodiode array detector (Princeton Applied Research, Model 1461.88 interface). The detector was thermoelectrically cooled to 5°C. This detector was designed to provide low-stray light and a flat undistorted focal plane ideal for sensitive work. The overall system offers a unique approach for real-time data acquisition of samples with low Raman scattering cross sections. An increase in data acquisition up to three orders of magnitude is possible over the standard photomultiplier tube. The detector achieves this speed by accepting a wide band of energy units at one time, somewhat like an electronic photographic plate.

The grating configuration used in this study (1800 gr/mm), allows the detector to collect a window of scattered Raman frequencies over a energy band width of approximately 825 cm^{-1}. It is possible to obtain Raman information from a strong scatterer, like TiO_2 (anatase), in 30 milliseconds (see the Appendix). The spectra obtained from PbO and As_2O_3 were recorded with a scan time of 2 and 1 seconds respectively. Recording times for this study varied between 30 milliseconds and 4 minutes. The grating remains stationary for a specific band width. The grating must be reset to another wavelength to obtain information outside

this band width. For this particular study, useful characteristic data were obtained for most crystalline materials within the energy window of 100 to 925 cm^{-1}. (Some materials may have additional bands outside of this window.) For a few select materials, the energy window was extended to 2000 cm^{-1}.

When working with single crystals, crystalline powders and thin films, elastically scattered light from the laser source is an unwanted problem. The desired information is in the inelastically scattered light. The Spex 1877E monochromators effectively eliminate a majority of the elastically scattered radiation; however, correct presentation of the sample to the laser beam can greatly enhance the effectiveness of the spectrometer. The incoming laser beam is focused on the sample surface as shown in Figure 1. The geometry of the sample holder places the sample surface at an angle of approximately 10° from the vertical. This setting places the surface of the sample at or below Brewster's angle and allows for maximum energy transfer to the sample and, consequently, optimum Raman scattering is achieved. The inelastically scattered energies were collected at 90° from the incident beam and focused by a lens onto the entrance slit of the monochromator. This holder was then attached to an X-Y-Z motion stage, shown in Figure 2. This configuration was found necessary to achieve optimum focus of the inelastically scattered light onto the first lens of the collection optics.

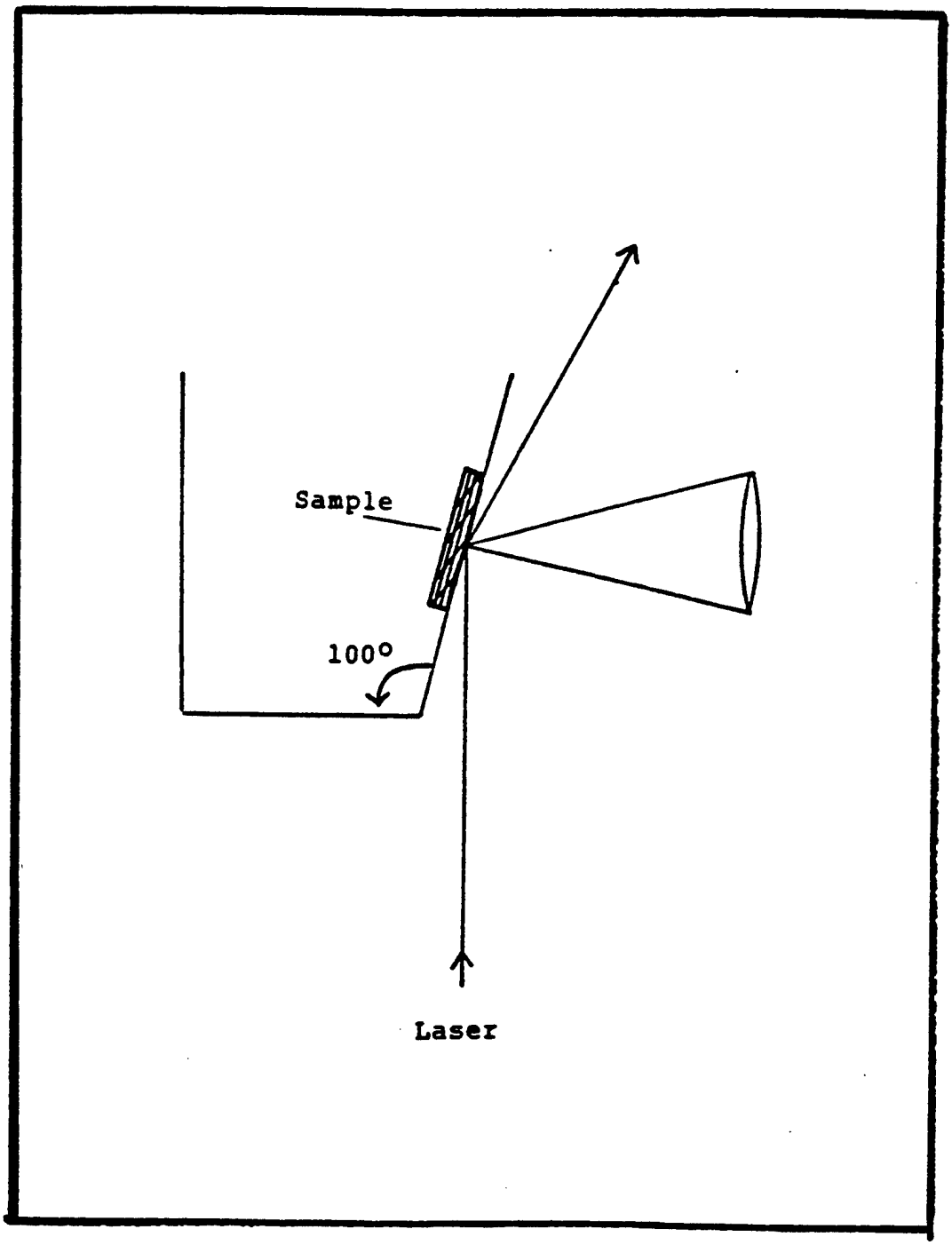


Figure 1. Scattering Geometry of Sample Holder.

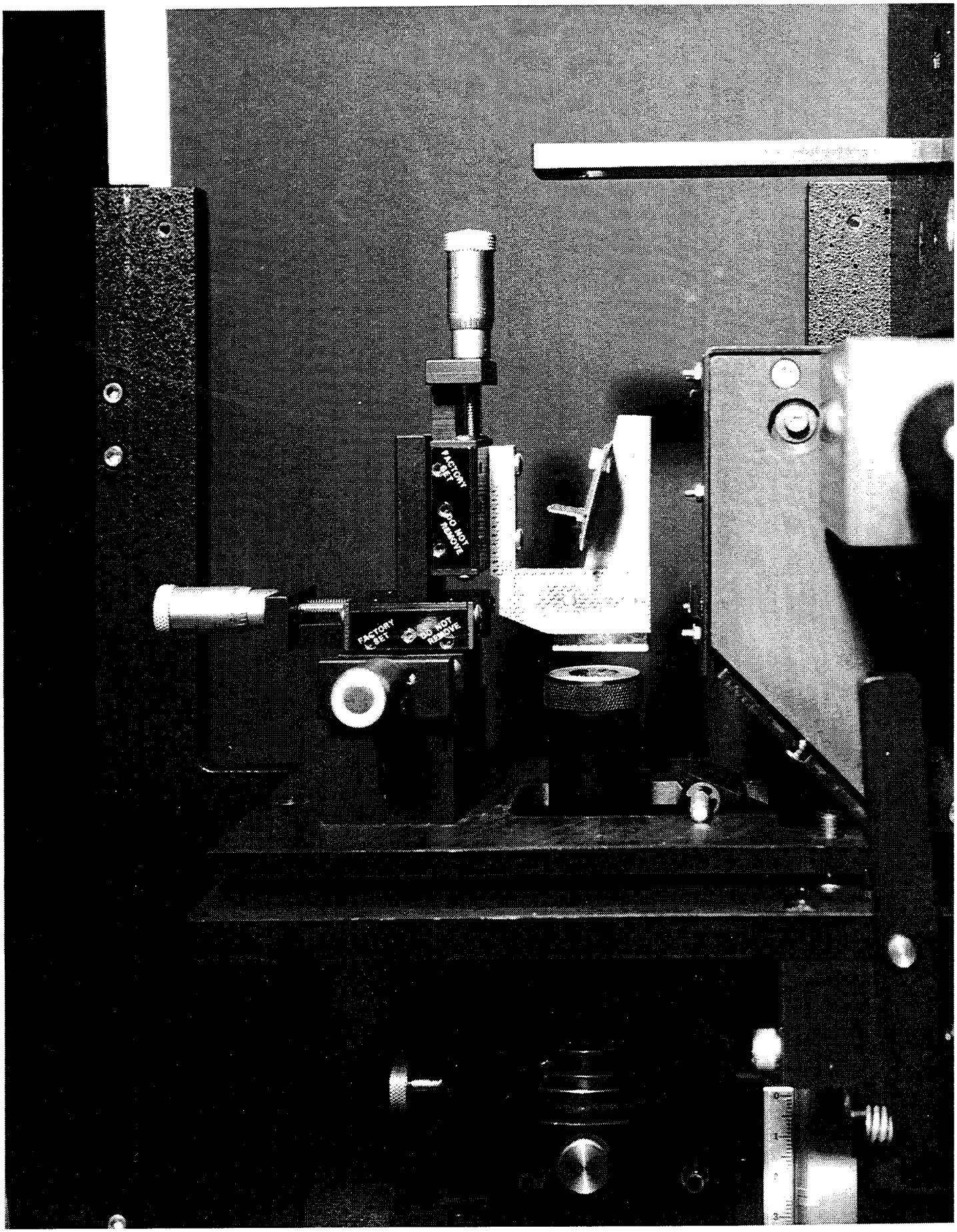


Figure 2. X - Y - Z Tripod for Sample Holder.

Section 3.0

Raman Spectra of Tribological Materials

3.1. Background

The main object of this paper is to present a library of Raman spectra of a number of inorganic materials that are related to tribological studies. The list is by no means all encompassing; however, it does provide a reasonable database for most studies. Only a general discussion concerning the information obtained from several specific compounds and their Raman spectra will be presented. The data for each spectrum in the library are generally presented with the strongest line shown at full scale. This method was chosen for ease in identifying materials from their recorded spectrum. However, each material has its own scattering cross section and a number of variables can affect the observed Raman intensities. Variables may be sample dependent or independent. Variables dependent on the individual sample are the refractive index and the interaction of the laser line with the material. Variables independent of the sample are the various instrument parameters, including the response of the detector and the spectral variation in the transmittance of the monochromators. The independent variables are only a problem when trying to compare intensity data from different instruments.

Table 2 shows the relative Raman scattering cross section of some materials studied in this paper.

TABLE 2

Relative Raman Scattering Cross Section

Sample	Scale
MoO_3	100
Sulfur	100
Sb_2O_3	25
PbO	15
MoS_2	1

All the samples were recorded under identical instrument conditions. The numbers represent a scale for scattering sensitivity, with 100 representing the compounds having the largest scattering cross section [Ref 7].

In order to minimize the sample variables, each sample was prepared so the spectral characteristics of each powder gave reproducible results. The spectral characteristics were frequency position, band width, and relative intensity of the bands within the same sample. All of the materials studied, with the exception of one, were stable in the laser beam up to 150 mW. The one exception was Pb_3O_4. A freshly pressed sample showed a tendency to convert to PbO over a period of time at 150 mW. At 300 mW this sample would convert to PbO in a very short time.

3.2 Molybdenum Disulfide Studies

Molybdenum disulfide has been shown considerable interest as a solid lubricant. Its lubricant properties are attributed to its "layer lattice"

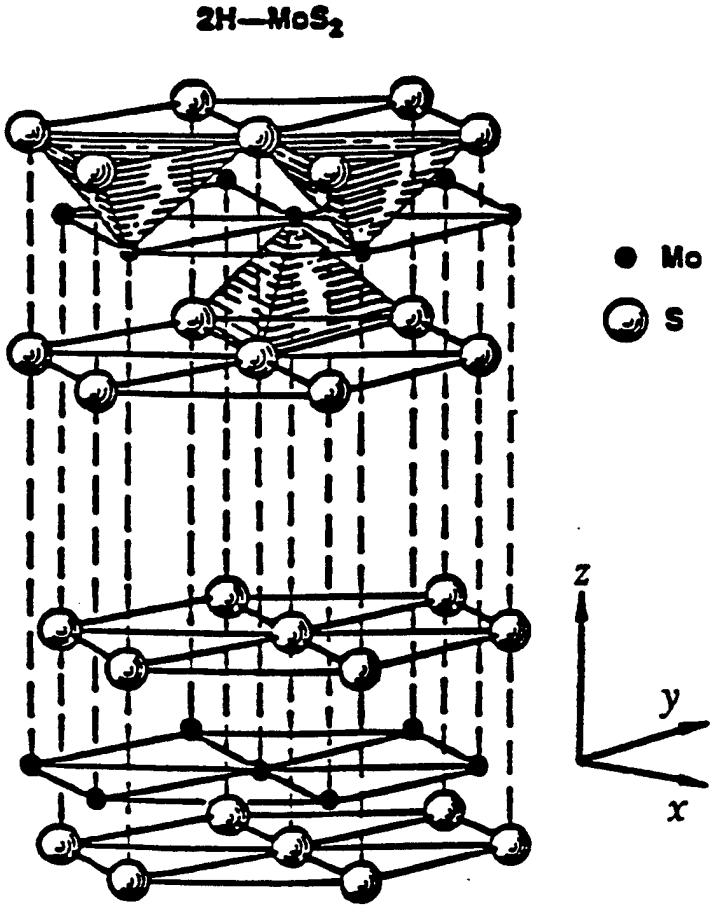


Figure 3. Crystal Structure of MoS_2.

structure, as diagrammed in Figure 3. A sheet of molybdenum atoms is sandwiched between two sheets of sulfur atoms forming an individual layer parallel to the base of the hexagonal crystal. These individual layers are stacked on top of each other and can be cleaved with extreme ease. This physical characteristic has led to the proposition that the individual layers contain strong bonds while the bonding between layers is weaker.

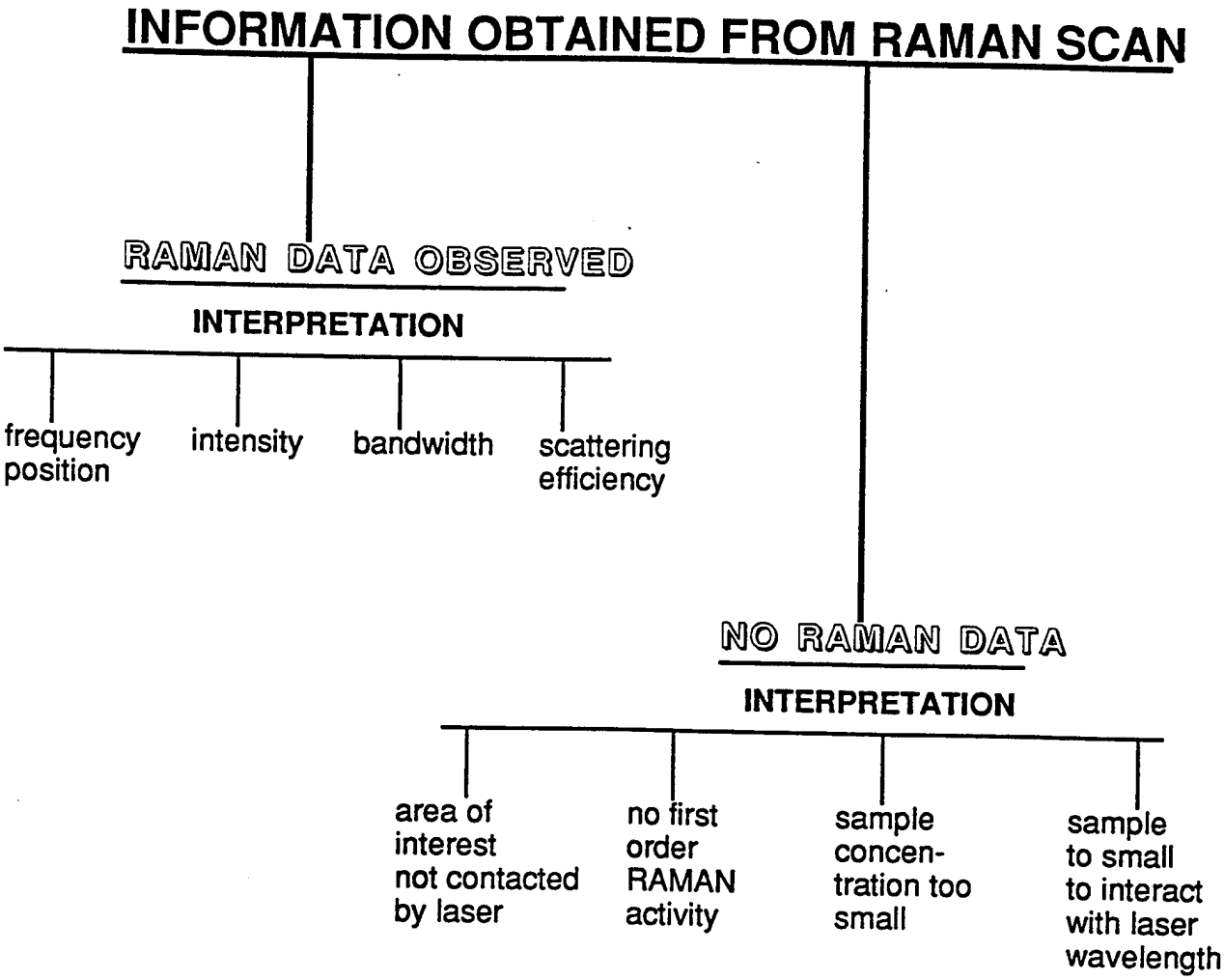
The Bravais unit cell contains two of these molecular trigonal layers. The first order Raman activity is derived from this structure. A correlation method analysis of molybdenum disulfide has been performed. The results of this analysis predicts four first-order Raman active modes for hexagonal MoS_2, and their spectral activity is as follows:

$$A_{1g} + 2B_{1g} + 2E_{2g} + E_{1g}$$

The B_{1g} vibration is not active in this crystal, leaving four Raman active modes. Raman data for MoS_2 (see Appendix) were obtained from the region 100 to 900 cm^{-1}. The two modes of interest show well defined peaks at 383 and 408 cm^{-1}. Even though discreet motions of atom pairs do not exist in this lattice, these frequencies have been labeled according to Wieting's notation [Ref. 6] for the purpose of discussion. The 383 cm^{-1} frequency (E_{2g}) has been assigned to the motion of the Mo+S atoms in the x-y layered plane of the unit cell. The 408 cm^{-1} frequency (A_{1g}) is assigned to the motion of the S-atoms along the z-axis of the unit cell.

Table 3 shows a schematic outline of the information that may be obtained from a Raman scan. When studying reference materials with fixed instrument parameters, the frequency positions, intensities of the bands, bandwidths, and scattering efficiency should remain relatively

TABLE 3


INFORMATION OBTAINED FROM RAMAN SCAN
RAMAN DATA OBSERVED
INTERPRETATION
frequency position
intensity
bandwidth
scattering efficiency
NO RAMAN DATA
INTERPRETATION
area of interest not contacted by laser
no first order RAMAN activity
sample concen-tration too small
sample to small to interact with laser wavelength

constant. When subjected to various experimental conditions these individual properties of a compound may change; however, the observed change can lend itself to analytical information about the material being studied [Ref. 8, 9].

When no Raman scattering is observed from a sample, a number of interpretations can also add to the information about the material being studied. When dealing with thin films, the material may not be concentrated enough to support Raman scattering. When dealing with deposited films, the long-range order may be too small and will appear amorphous to the laser beam. When dealing with tribological films and wear tracks the laser beam must be correctly positioned to obtain viable information. If all of the appropriate conditions are met and the sample does not show first-order Raman bands, it could indicate a crystal structure that does not support Raman scattering (e.g. transition-metal borides, carbides and nitrides). In general this report gives techniques and hints, but success depends on experience, patience and experimentation.

3.3 Procedure for Obtaining the Reference Raman Spectra

The primary method for obtaining Raman data for this study was to use nonpolarized measurements on pressed powder samples. The majority of samples studied were at least chemically pure materials (99.9%). The crystallite size was usually in the range of 0.3 to 1.5 microns in order that the intensity of the Raman bands be reproducible when using the 514.5 nm green line as a laser source.

For convenience the spectra are presented in alphabetical order according to the compound formula. This Raman study was performed on powdered samples, and the information obtained is presented primarily for identification purposes. All of the Raman spectra were obtained at room temperature. Samples that were easily identifiable from X-ray powder diffraction files are notated with their crystal structure. Literature references are reported with most of the spectra. The ratio of the intensity of two bands within the same spectrum may be used as an analytical tool. Intensities of bands from different compounds are not comparable.

The Appendix contains 51 Raman spectra that form the basis of our spectral library.

Section 4.0
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Section 4.0

APPENDIX
51 Raman Spectra

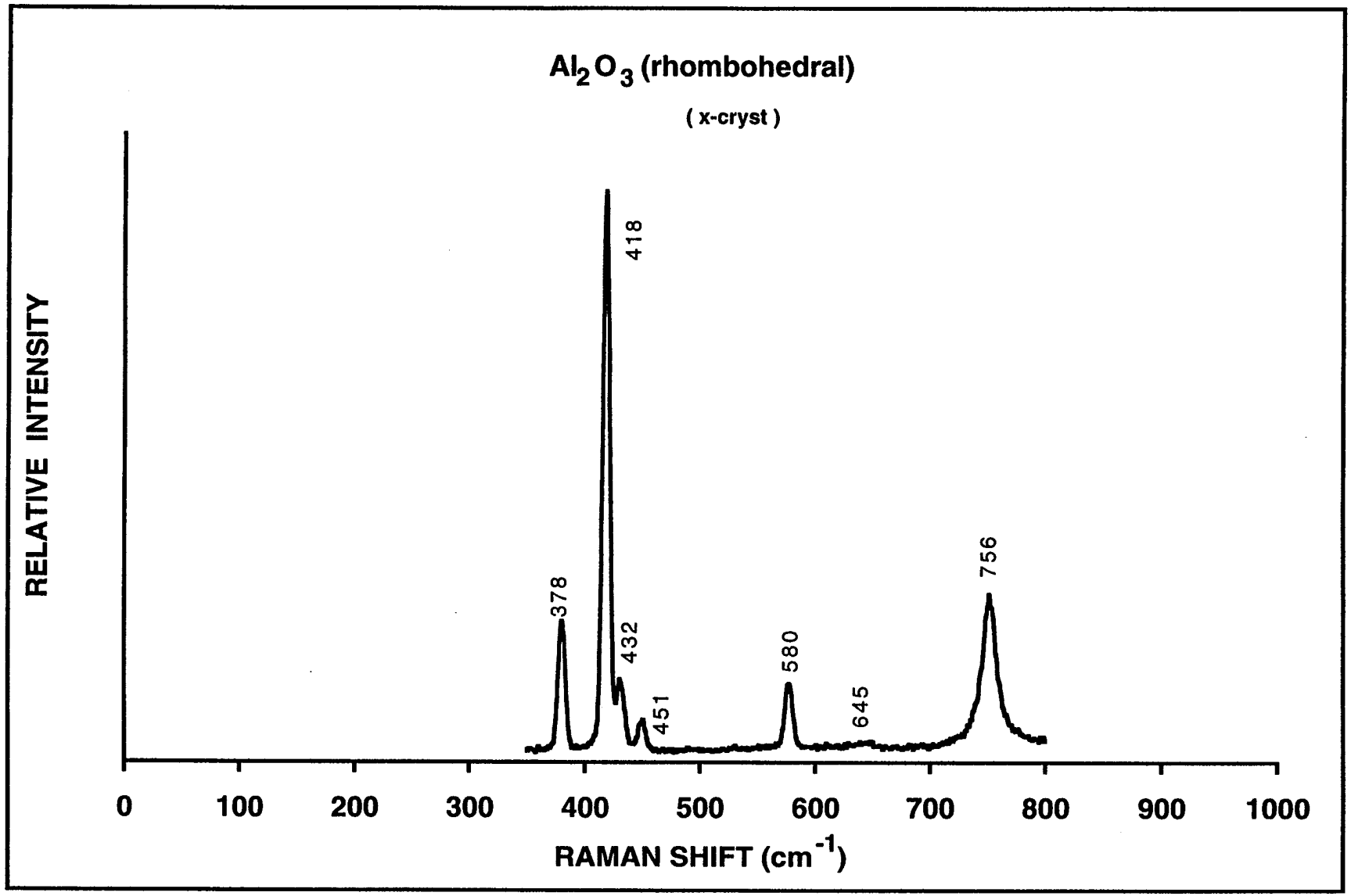

Figure A1. Raman Spectrum of Al2O3.

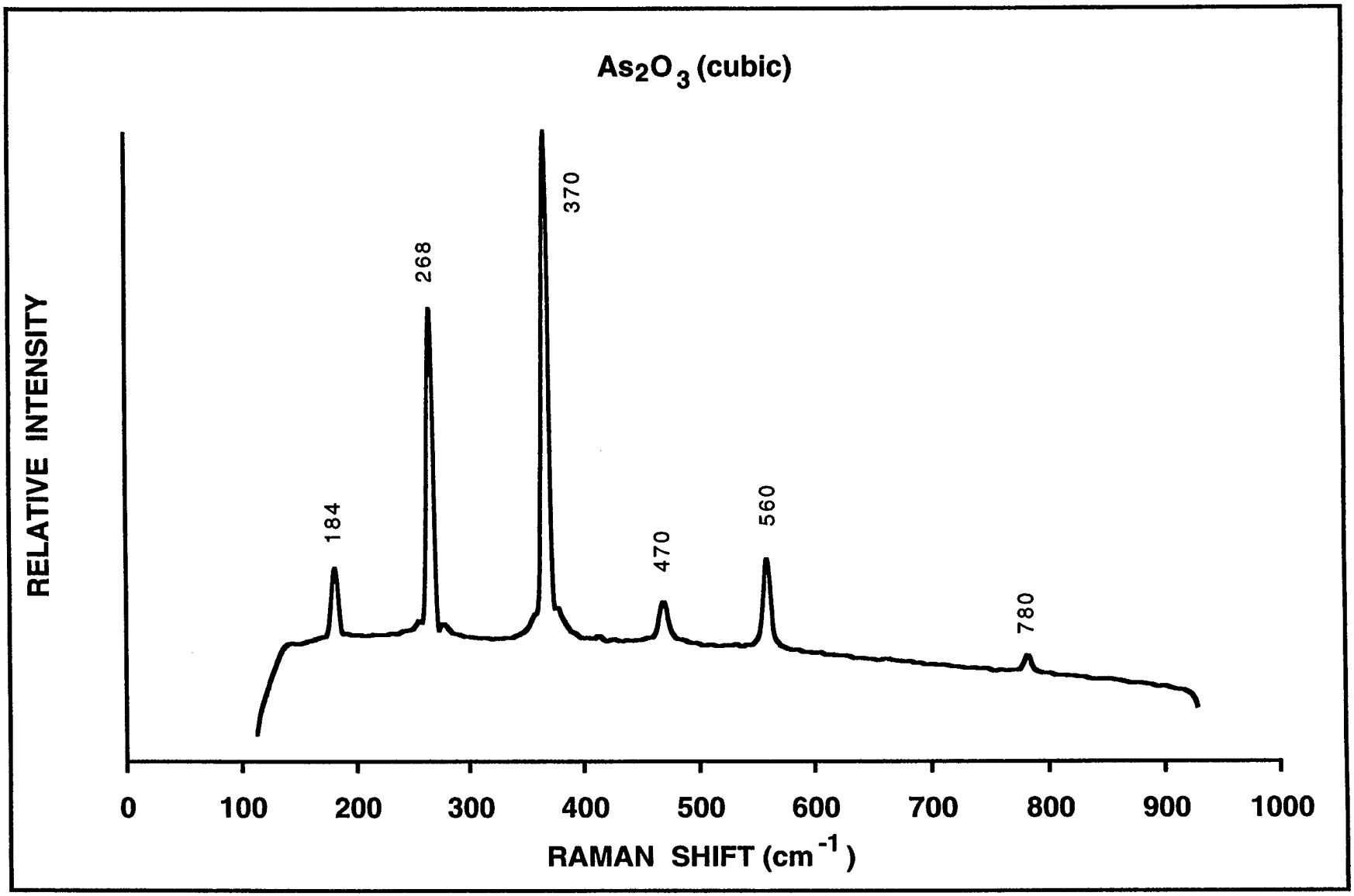

Figure A2. Raman Spectrum of As2O3.

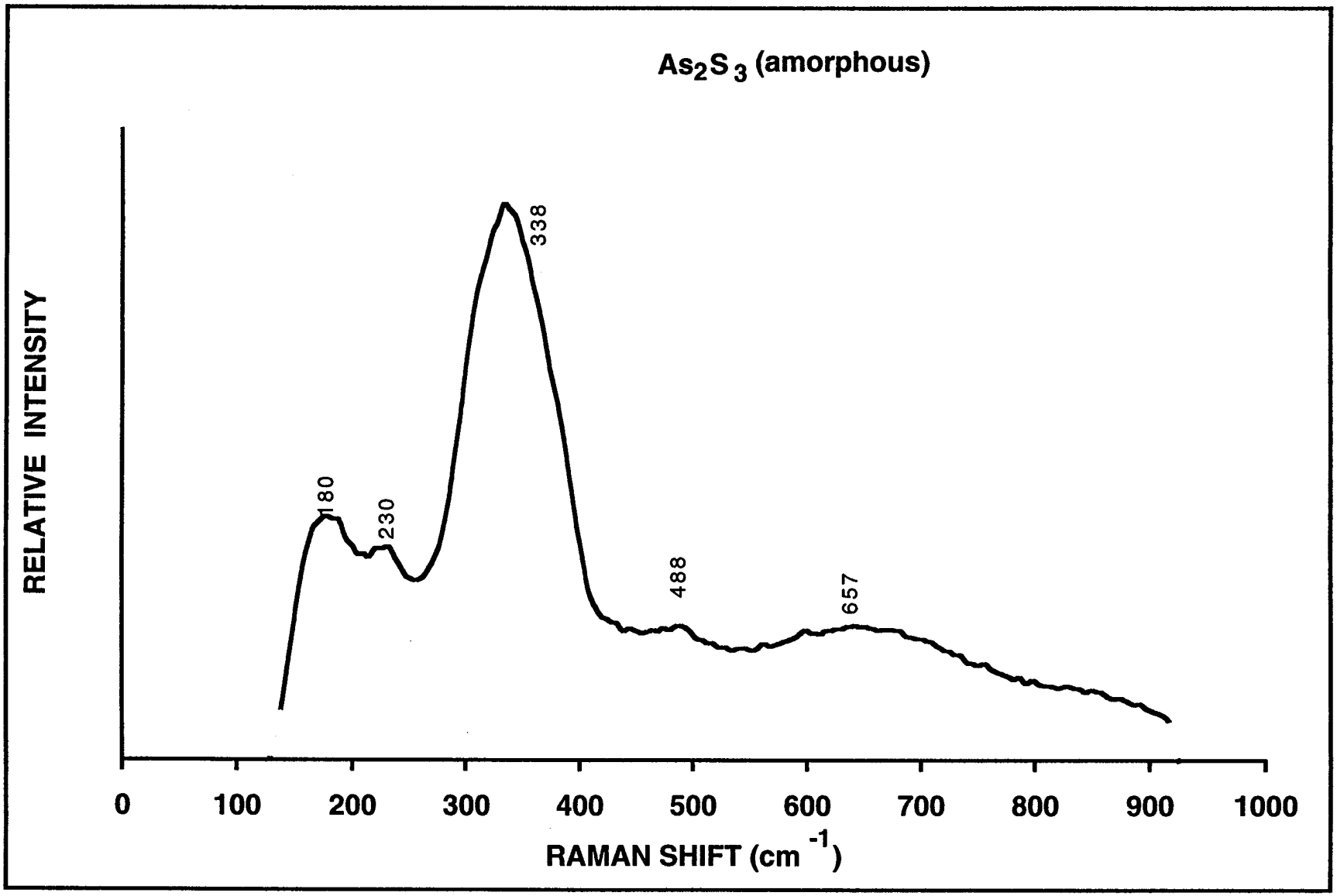

Figure A3. Raman Spectrum of As2S3.

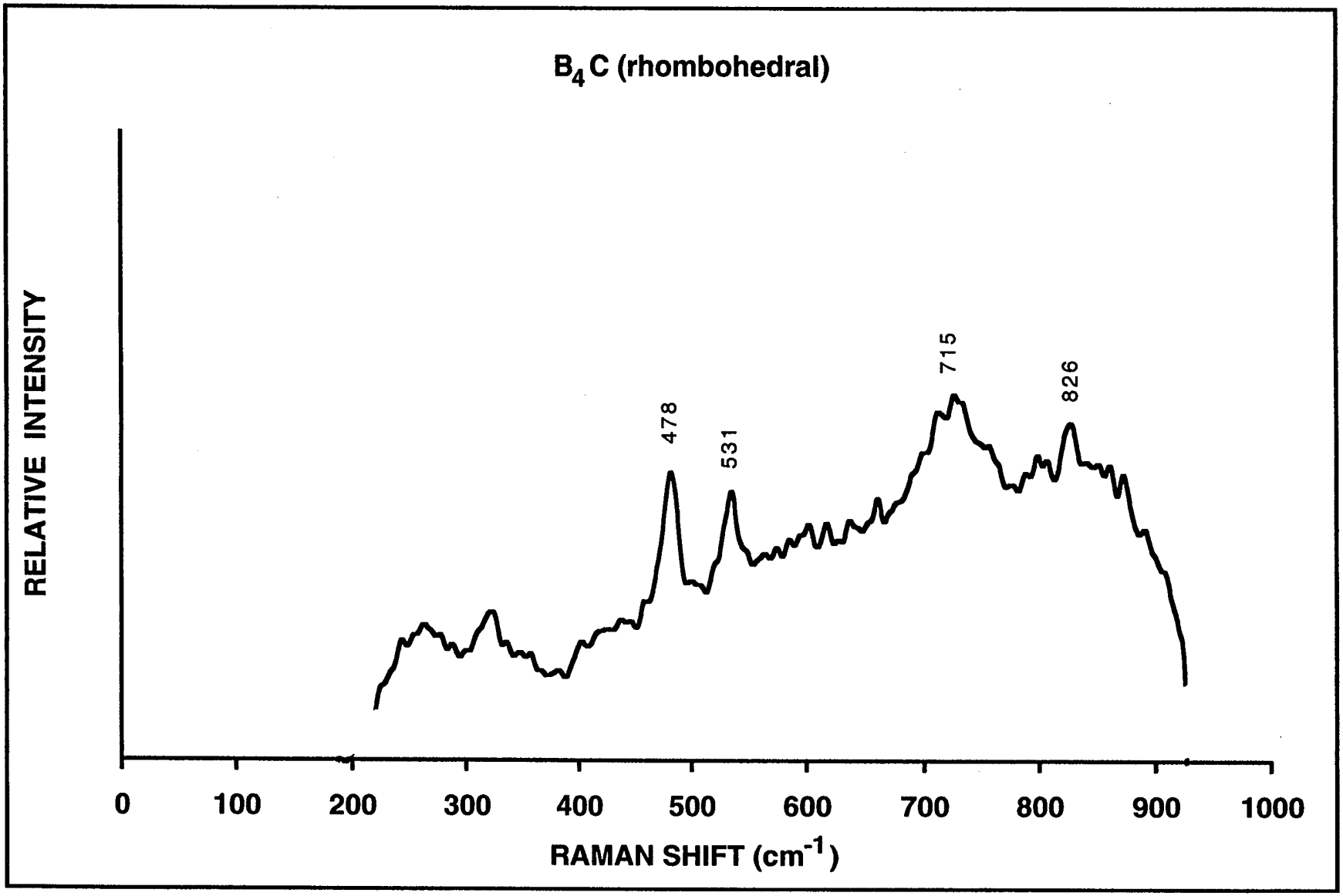

Figure A4. Raman Spectrum of B4C.

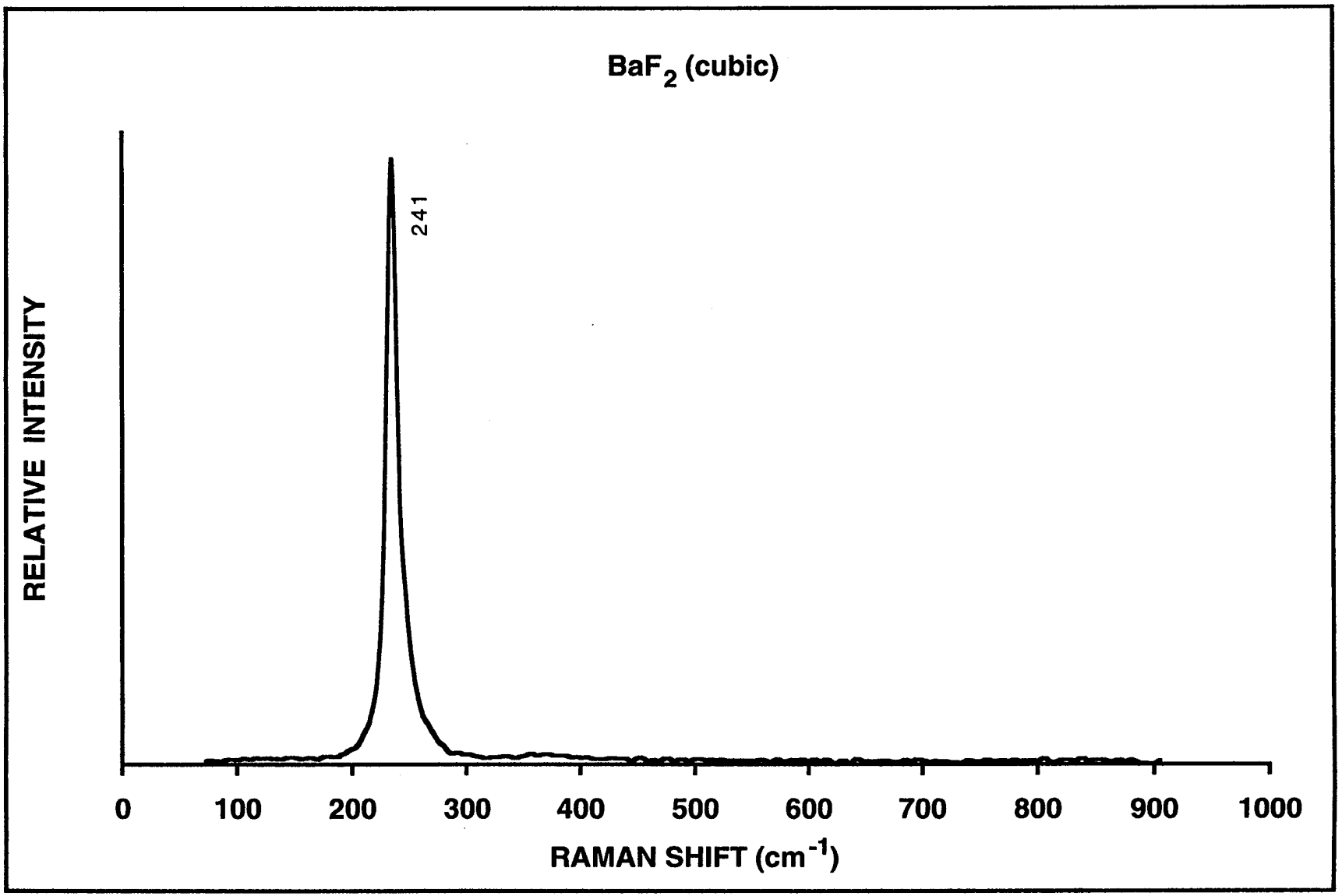

Figure A5. Raman Spectrum of BaF2.

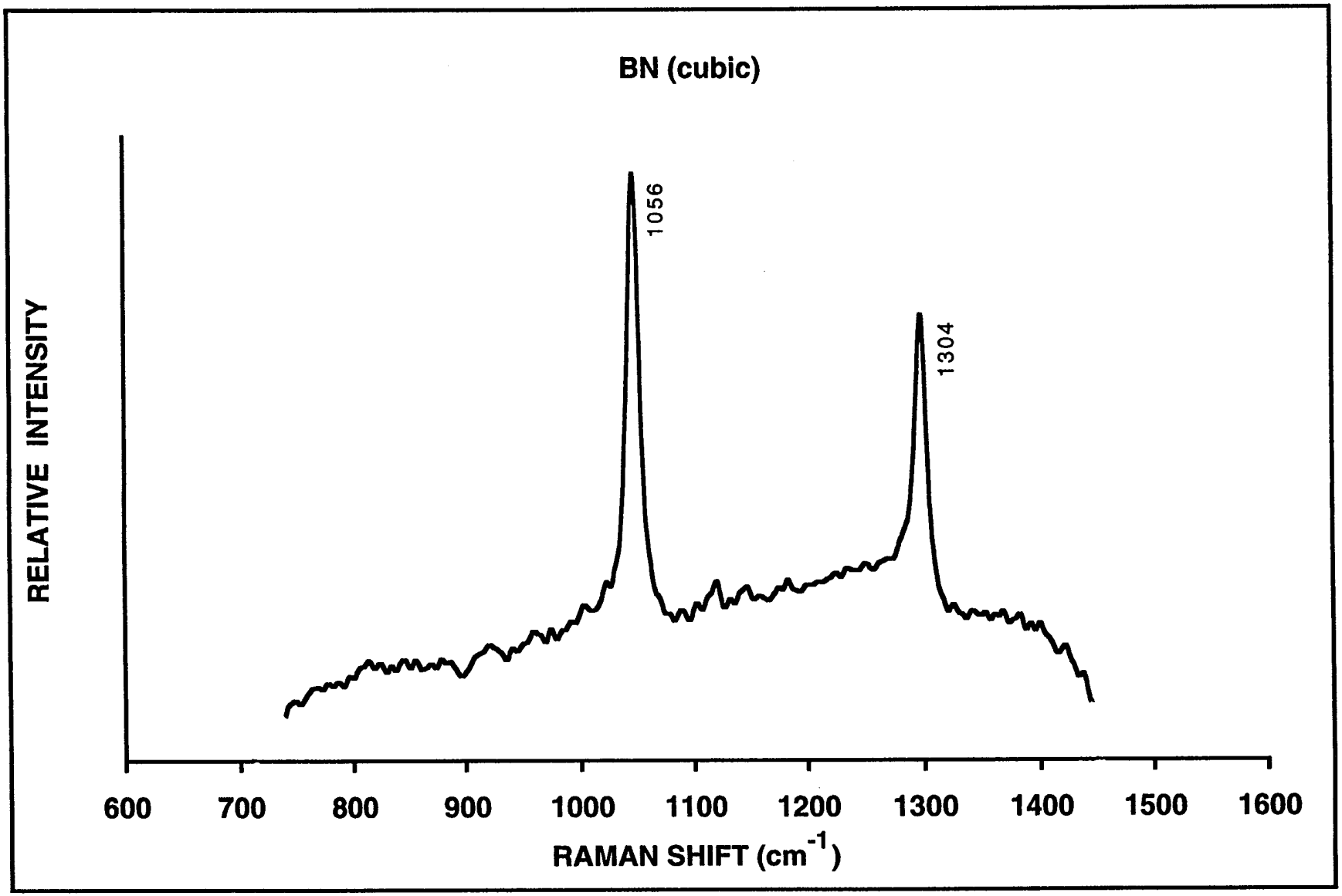

Figure A6. Raman Spectrum of BN.

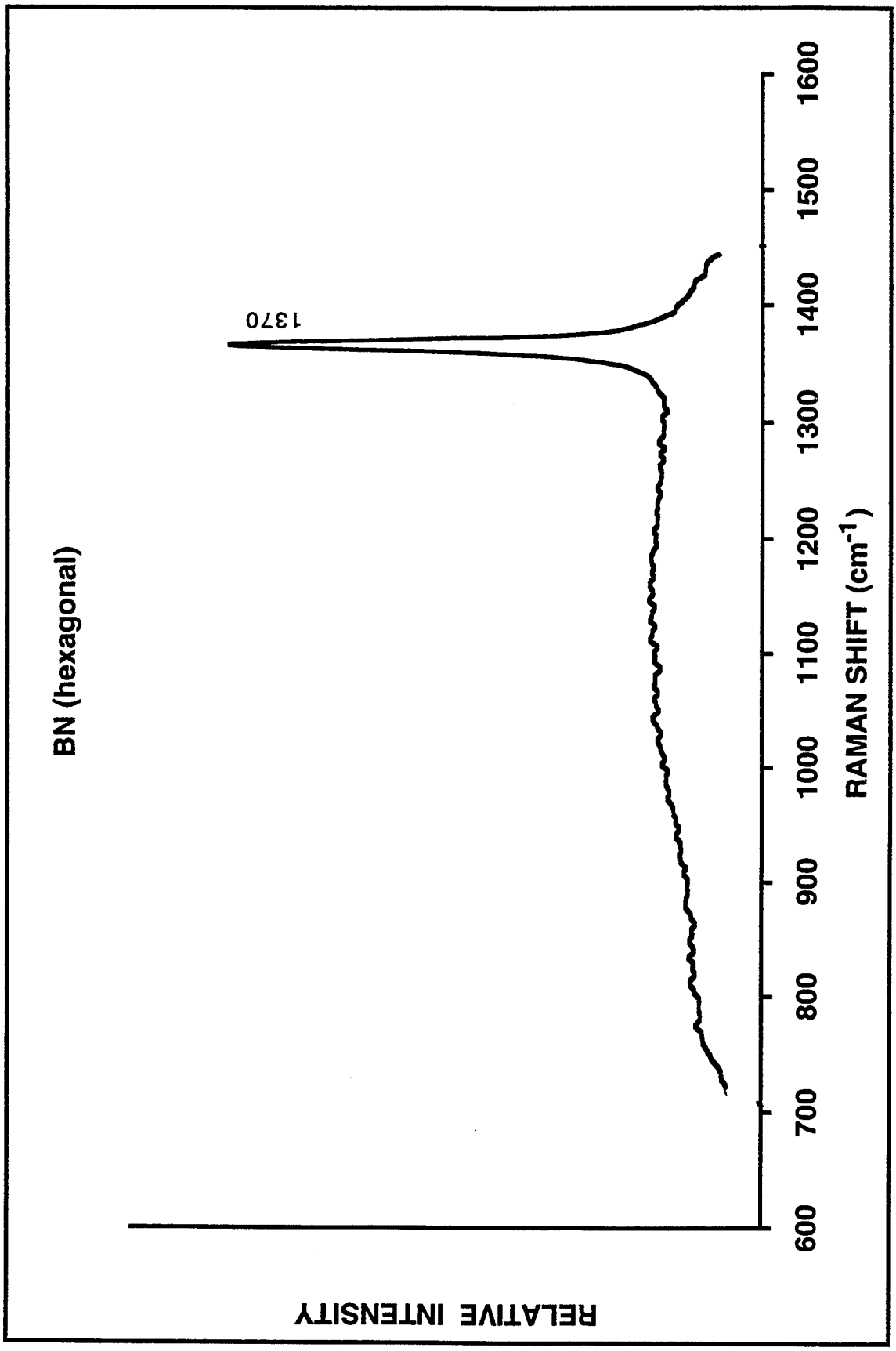

Figure A7. Raman Spectrum of BN.

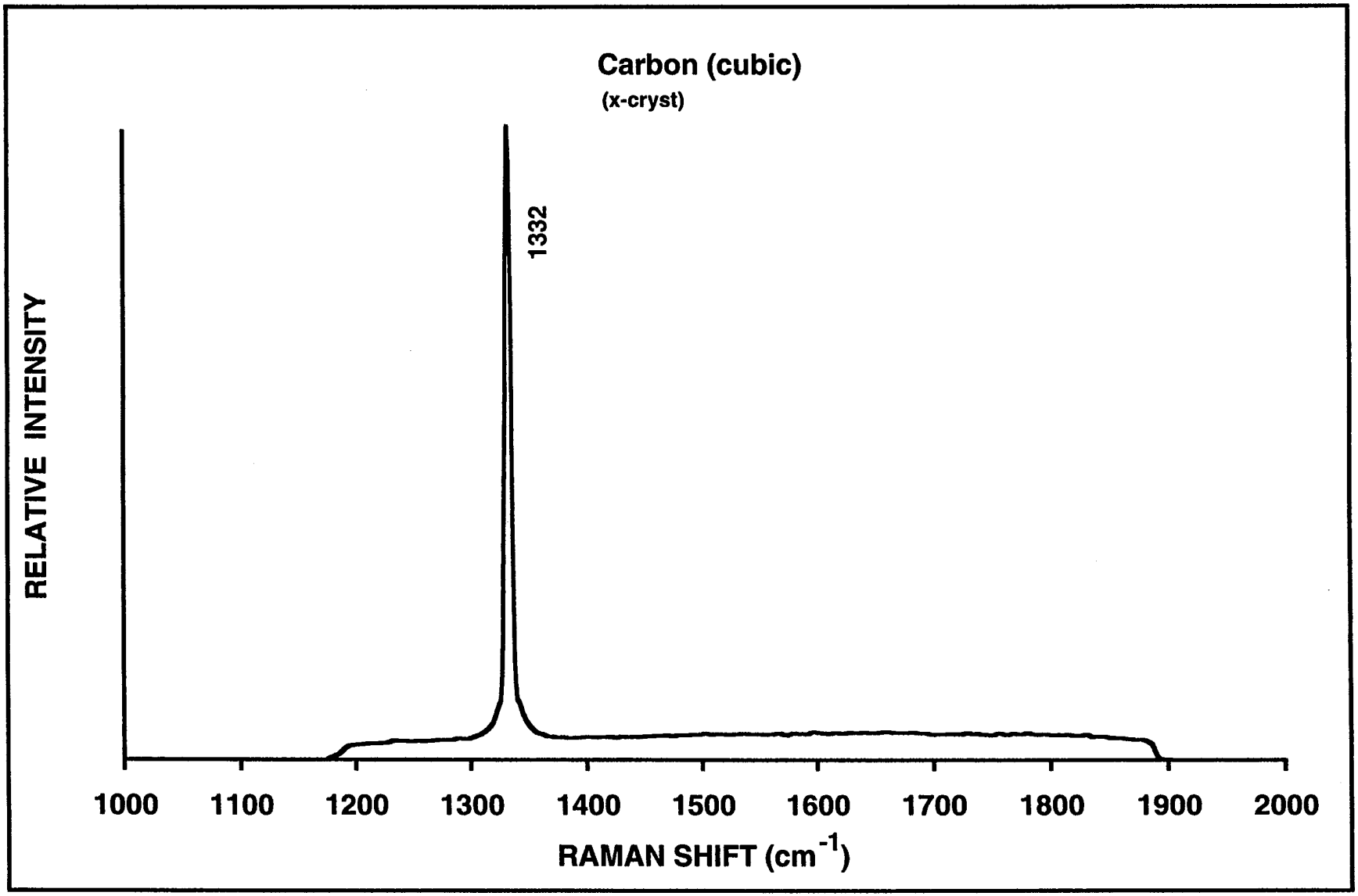

Figure A8. Raman Spectrum of Diamond.

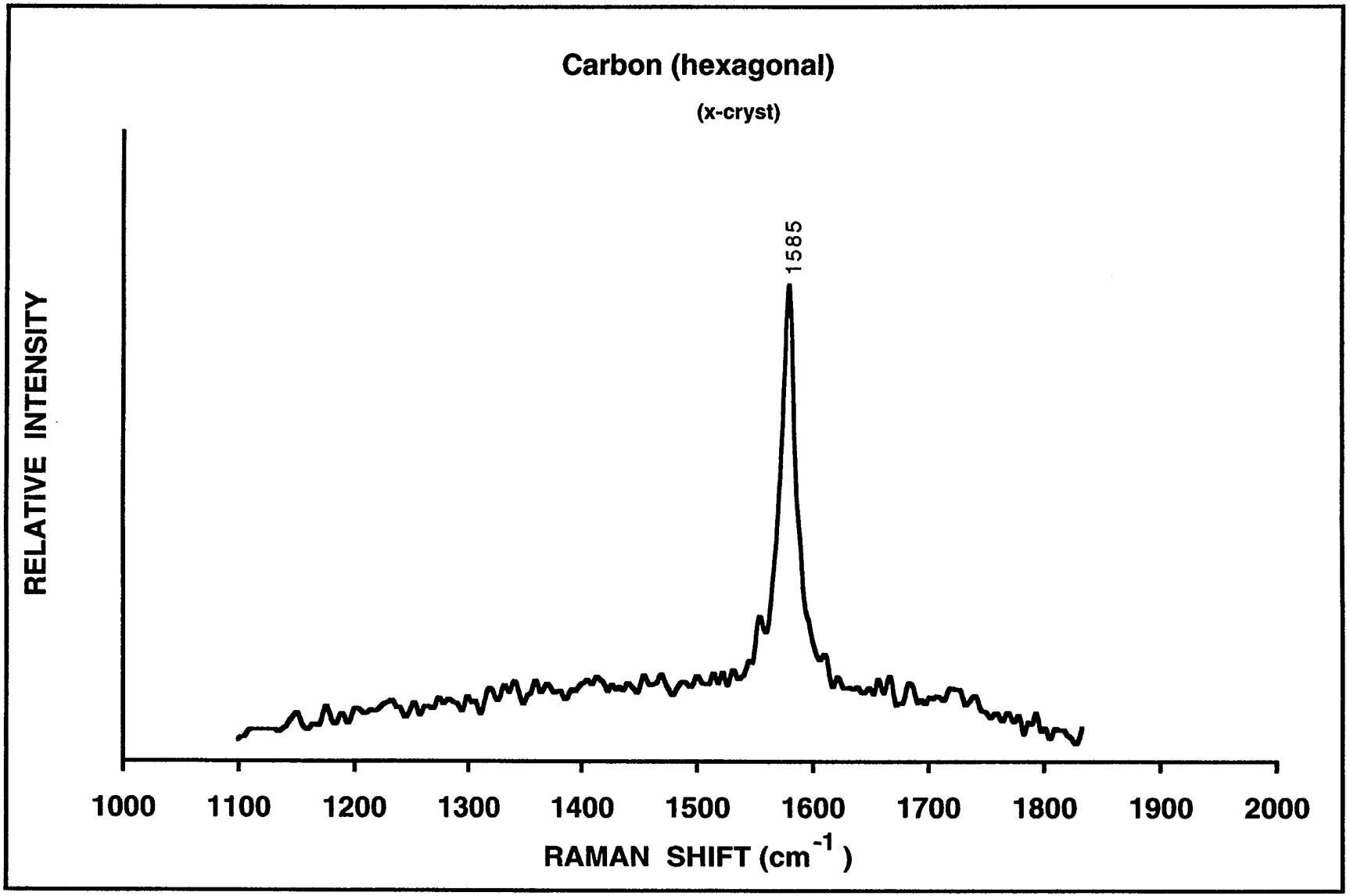

Figure A9. Raman Spectrum Of Graphite.

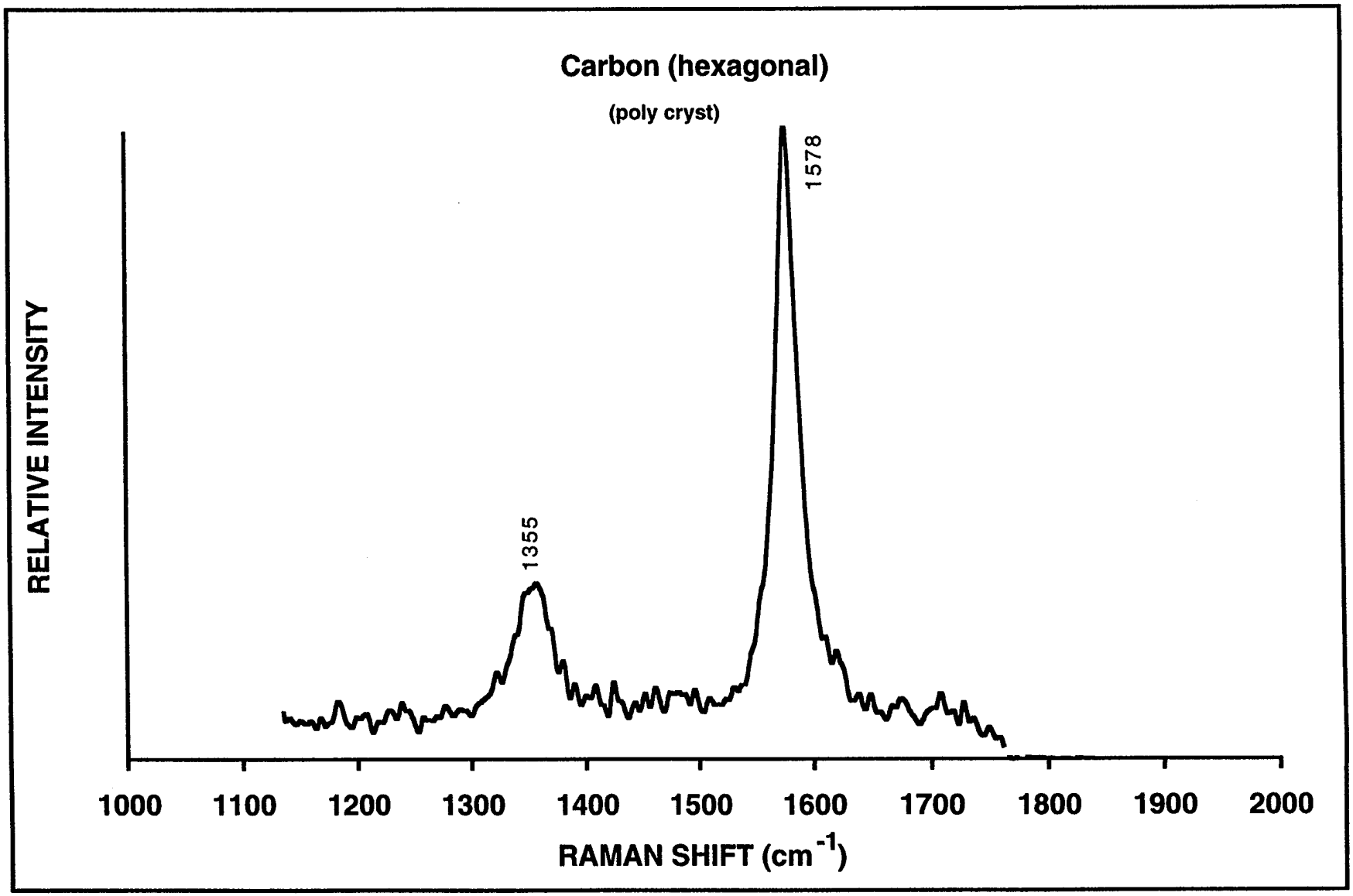

Figure A10. Raman Spectrum of Carbon.

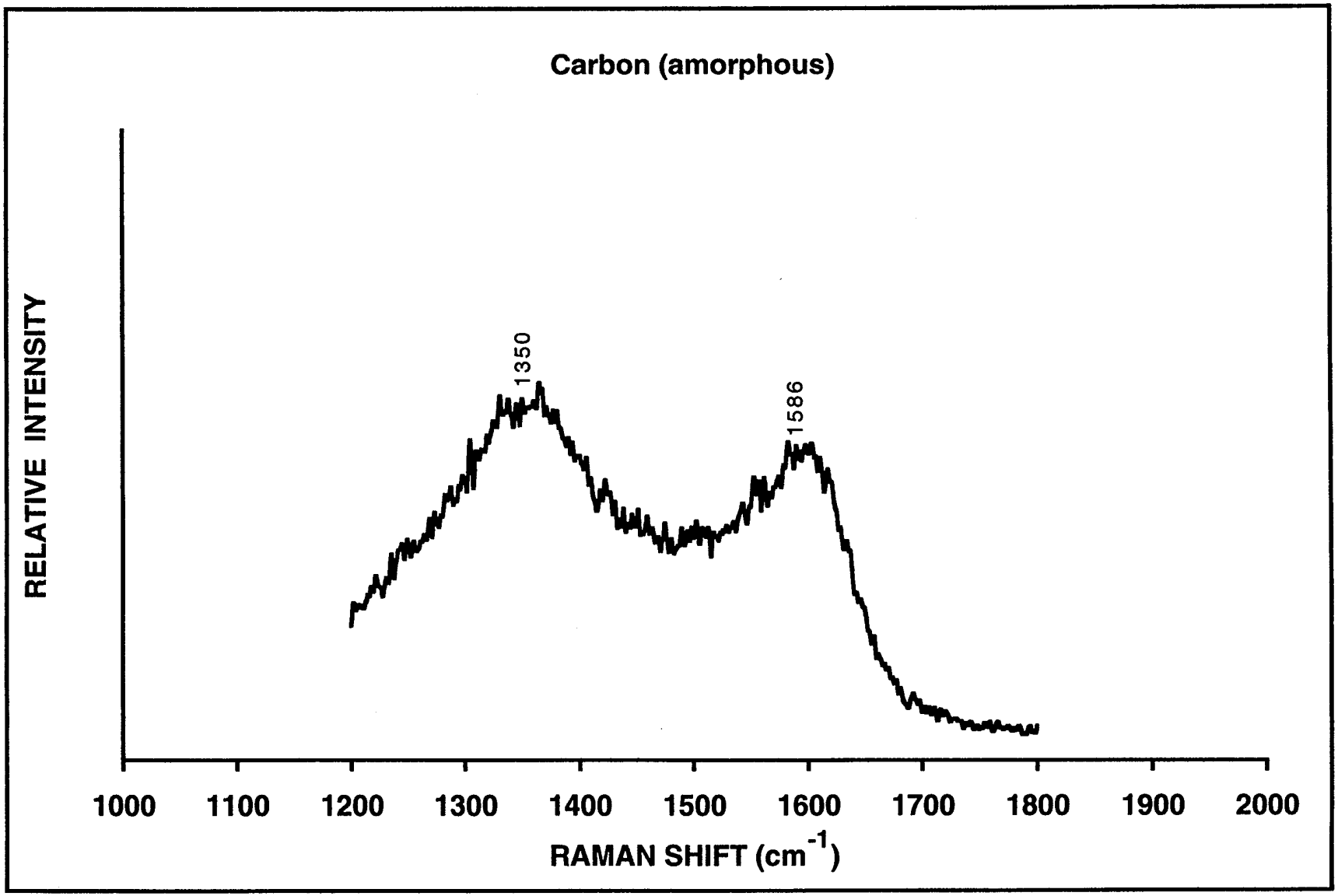

Figure A11. Raman Spectrum of Carbon.

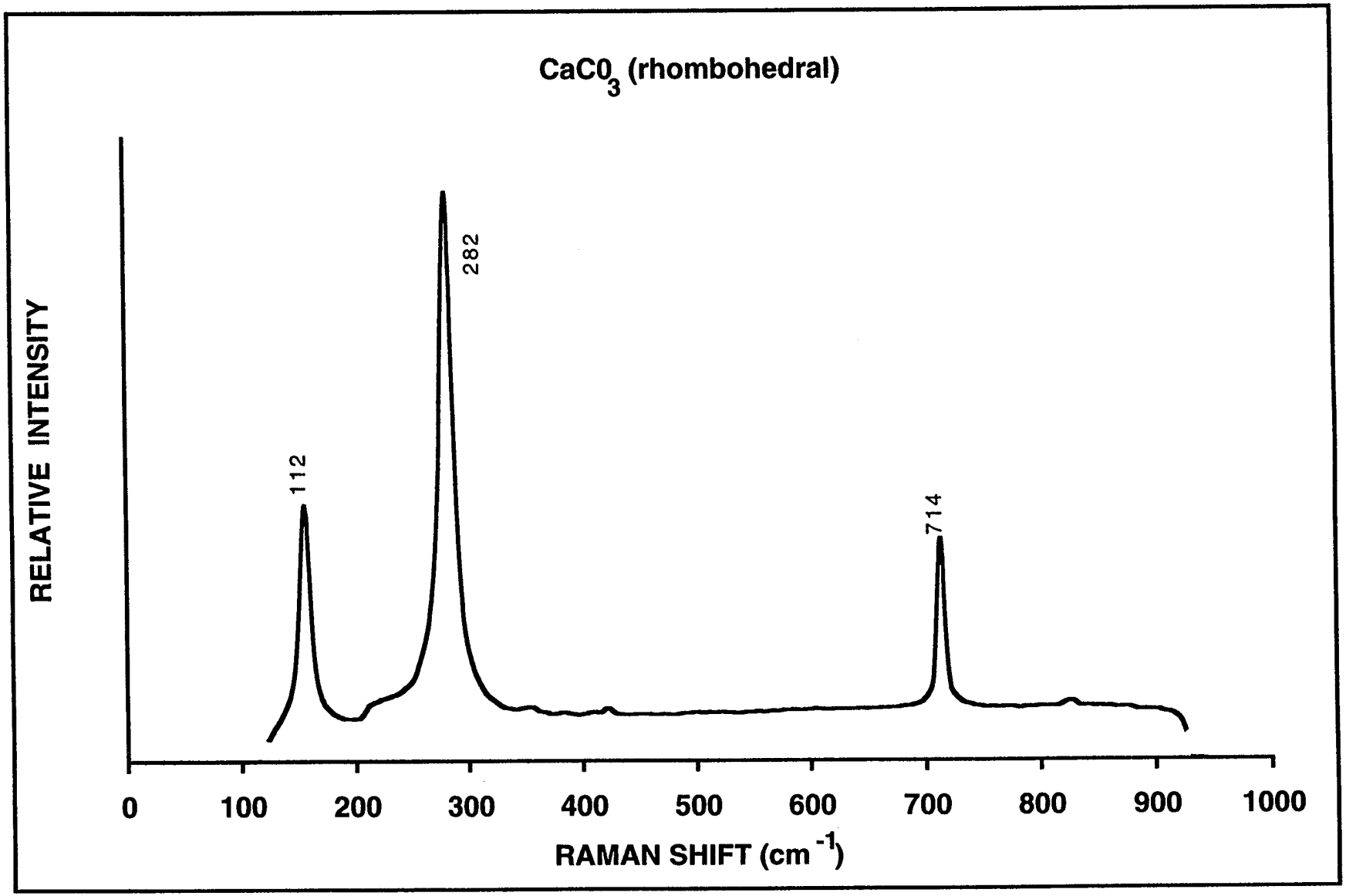

Figure A12. Raman Spectrum of CaCO3.

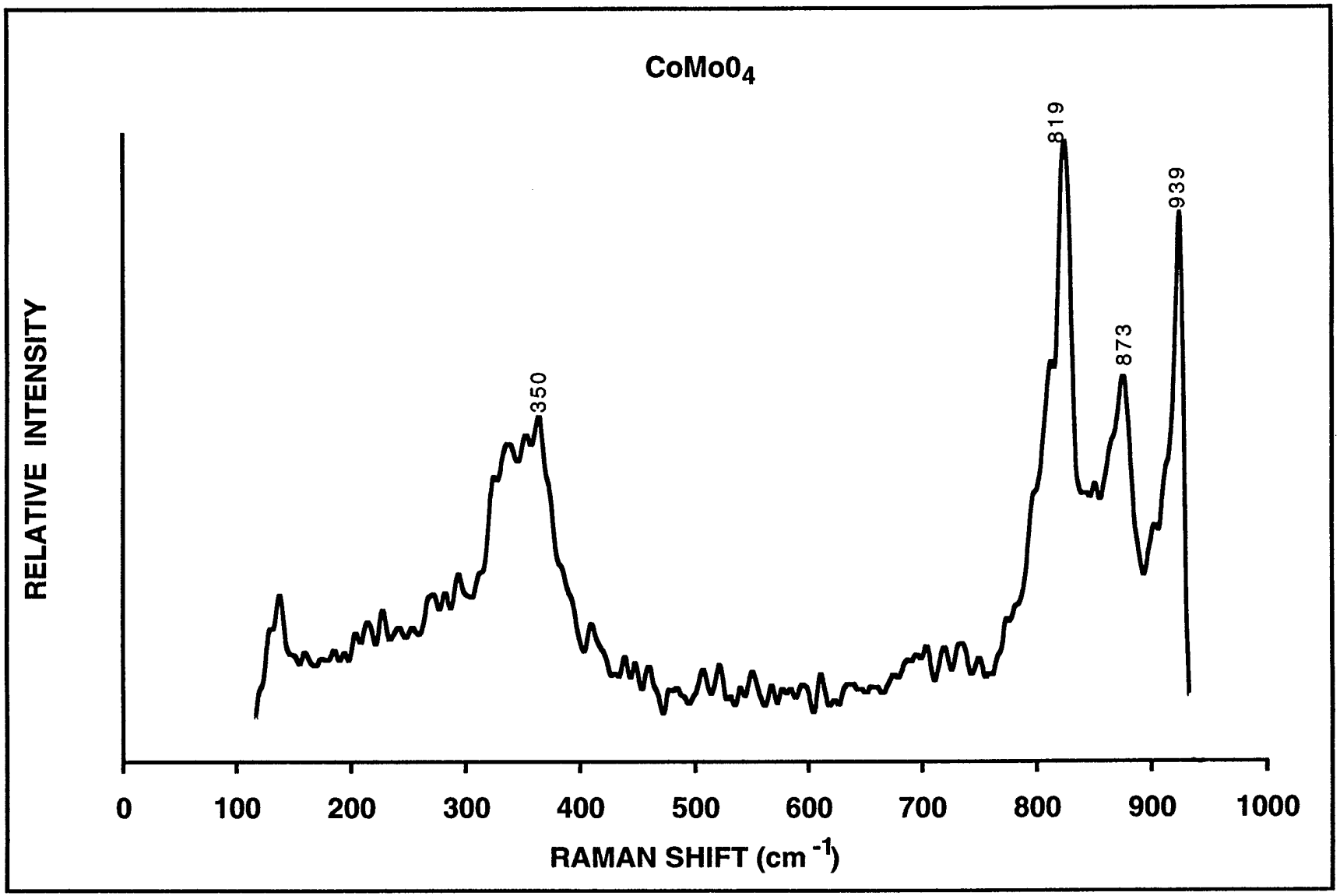

Figure A13. Raman Spectrum of CoMoO4.

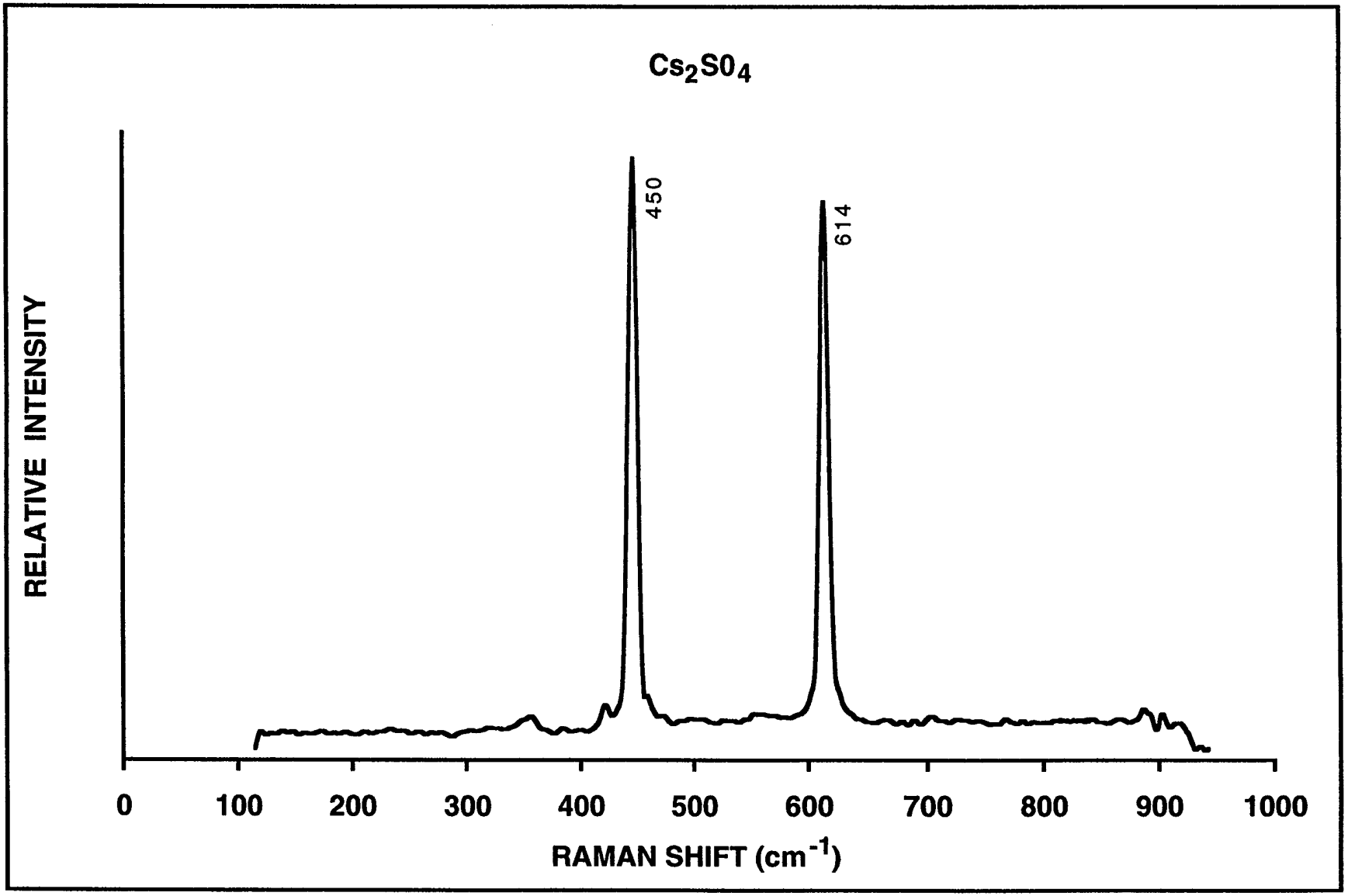

Figure A14. Raman Spectrum of Cs2SO4.

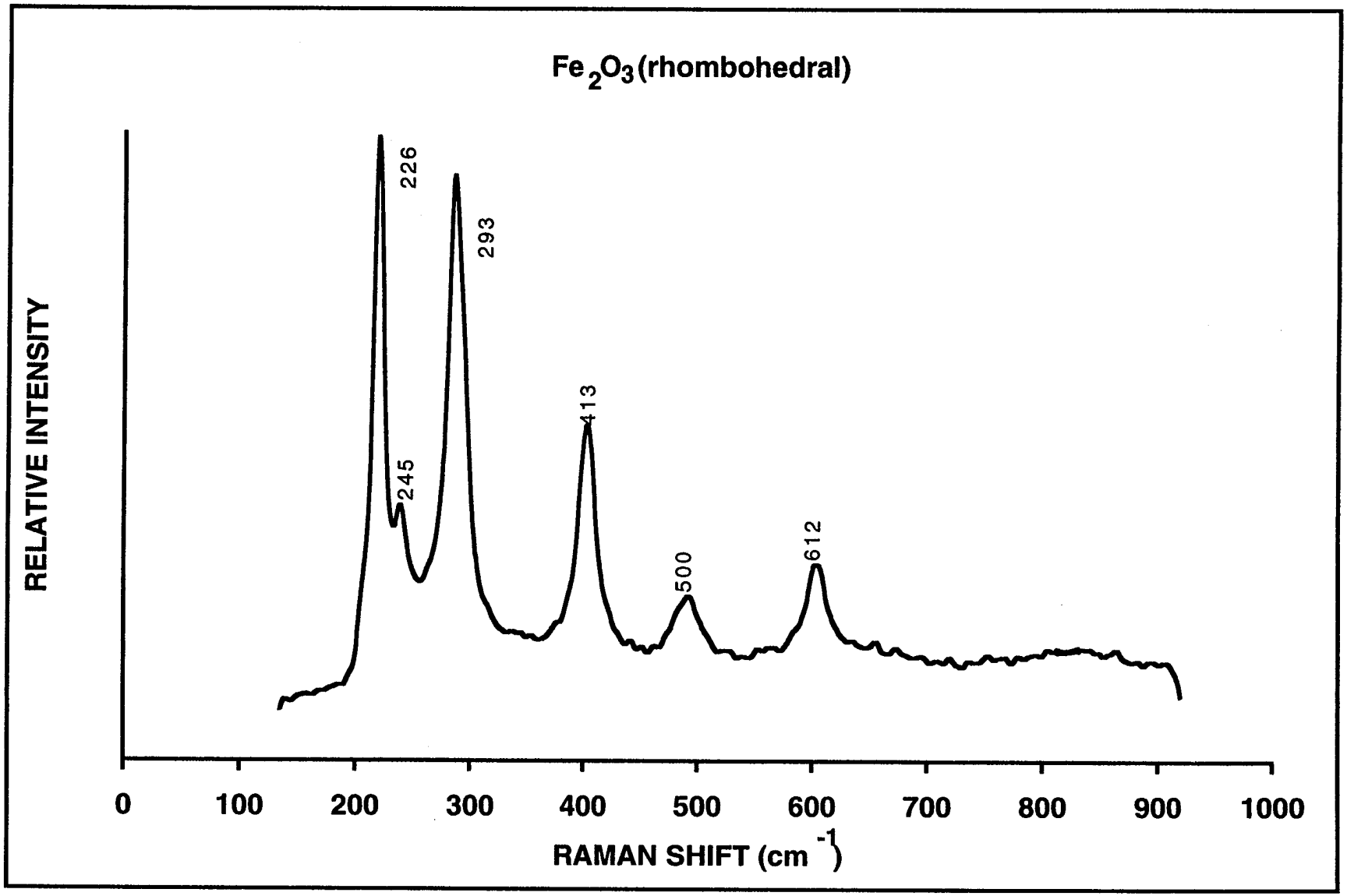

Figure A15. Raman Spectrum of Fe2O3.

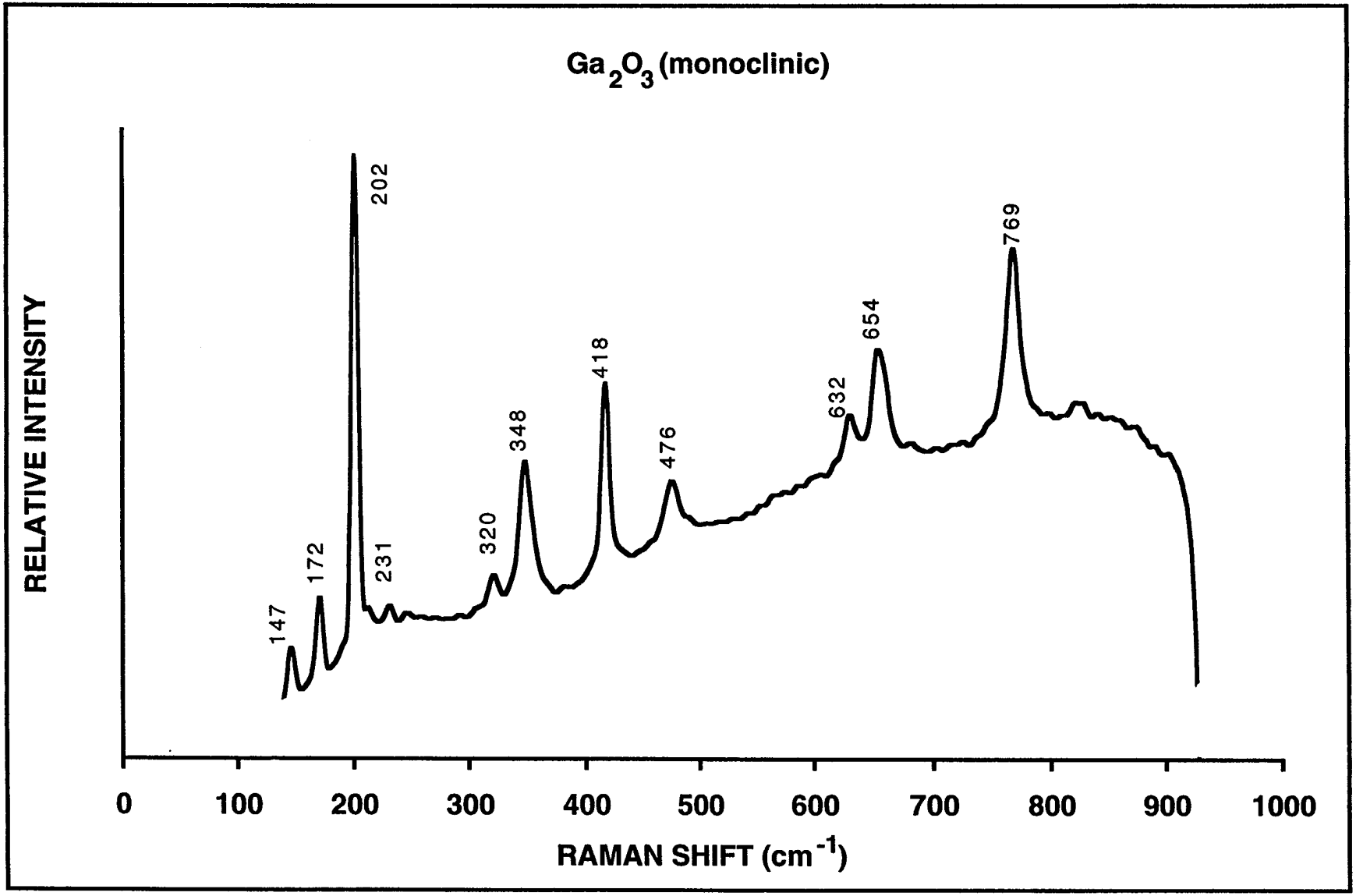

Figure A16. Raman Spectrm of Ga2O3.

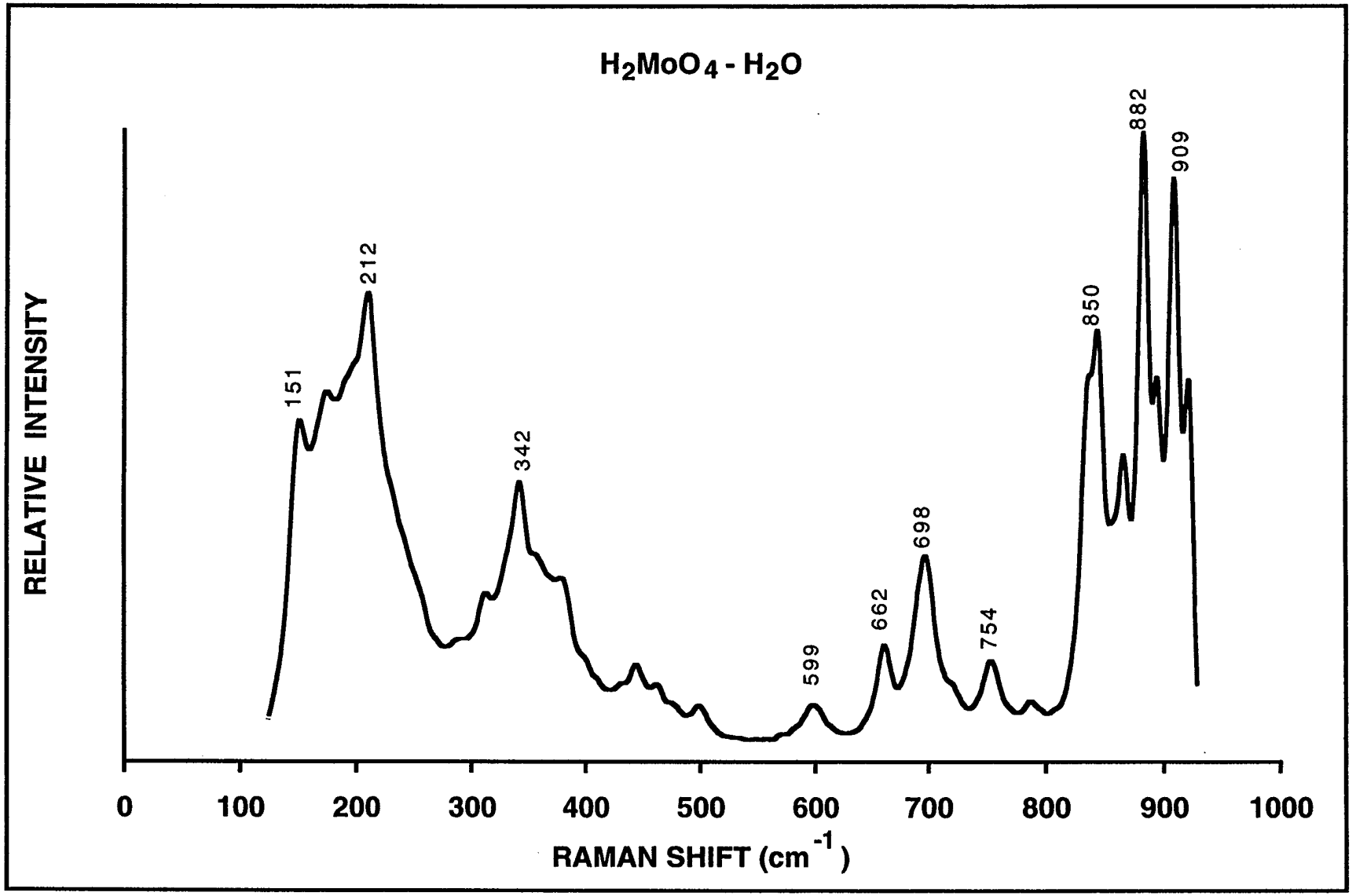

Figure A17. Raman Spectrum of H2MoO4.

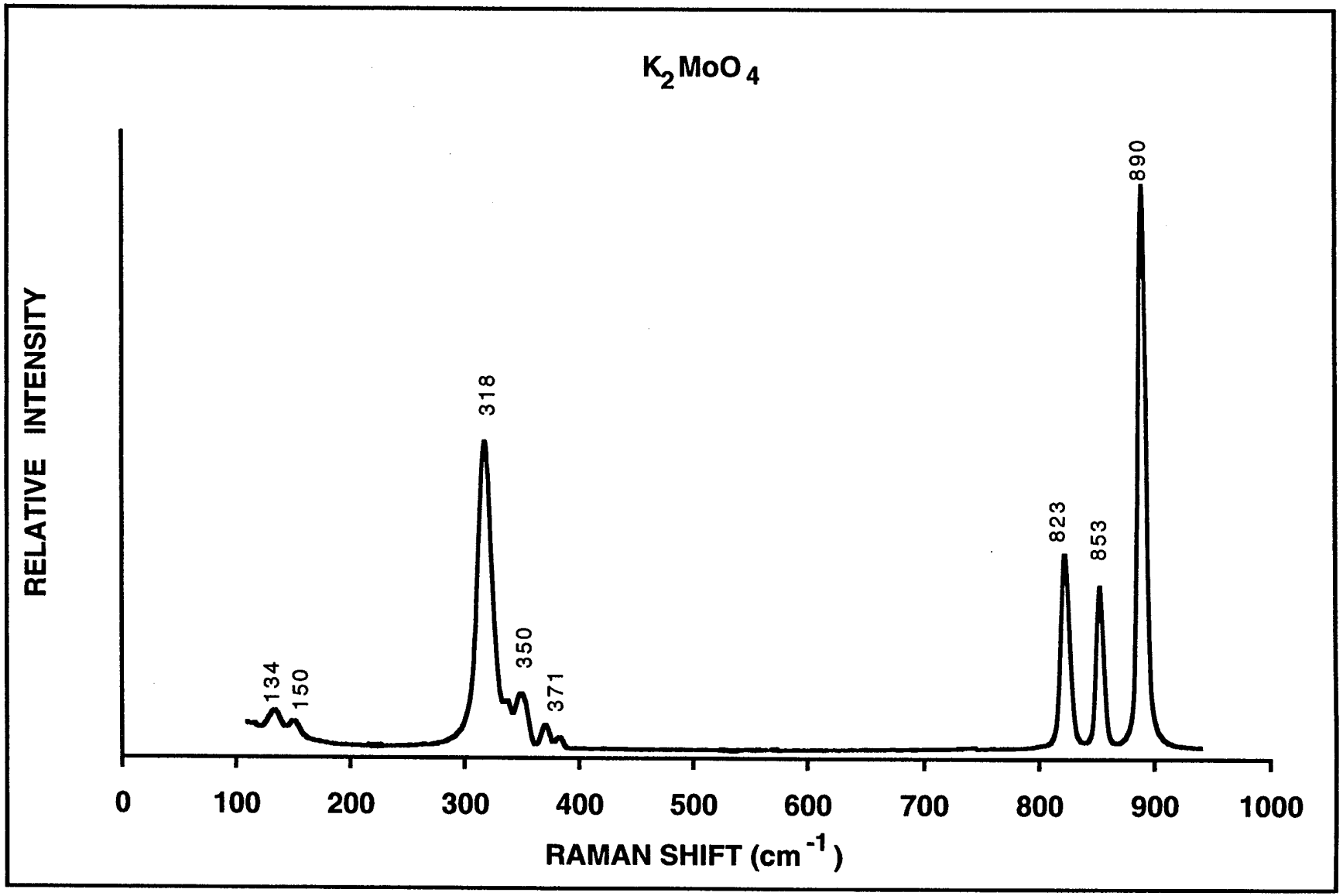

Figure A18. Raman Spectrum of K2MoO4.

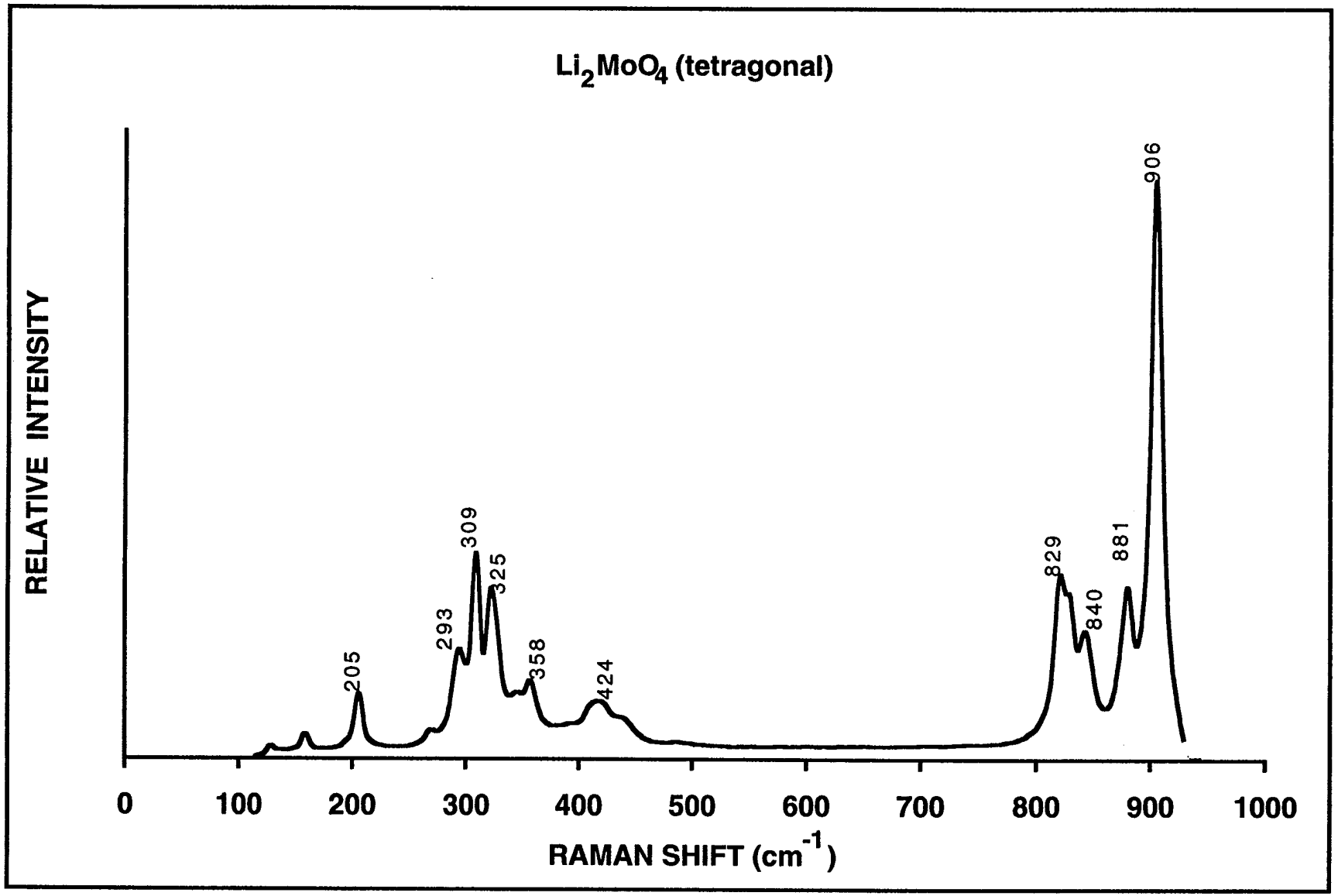

Figure A19. Raman Spectrum of Li2MoO4.

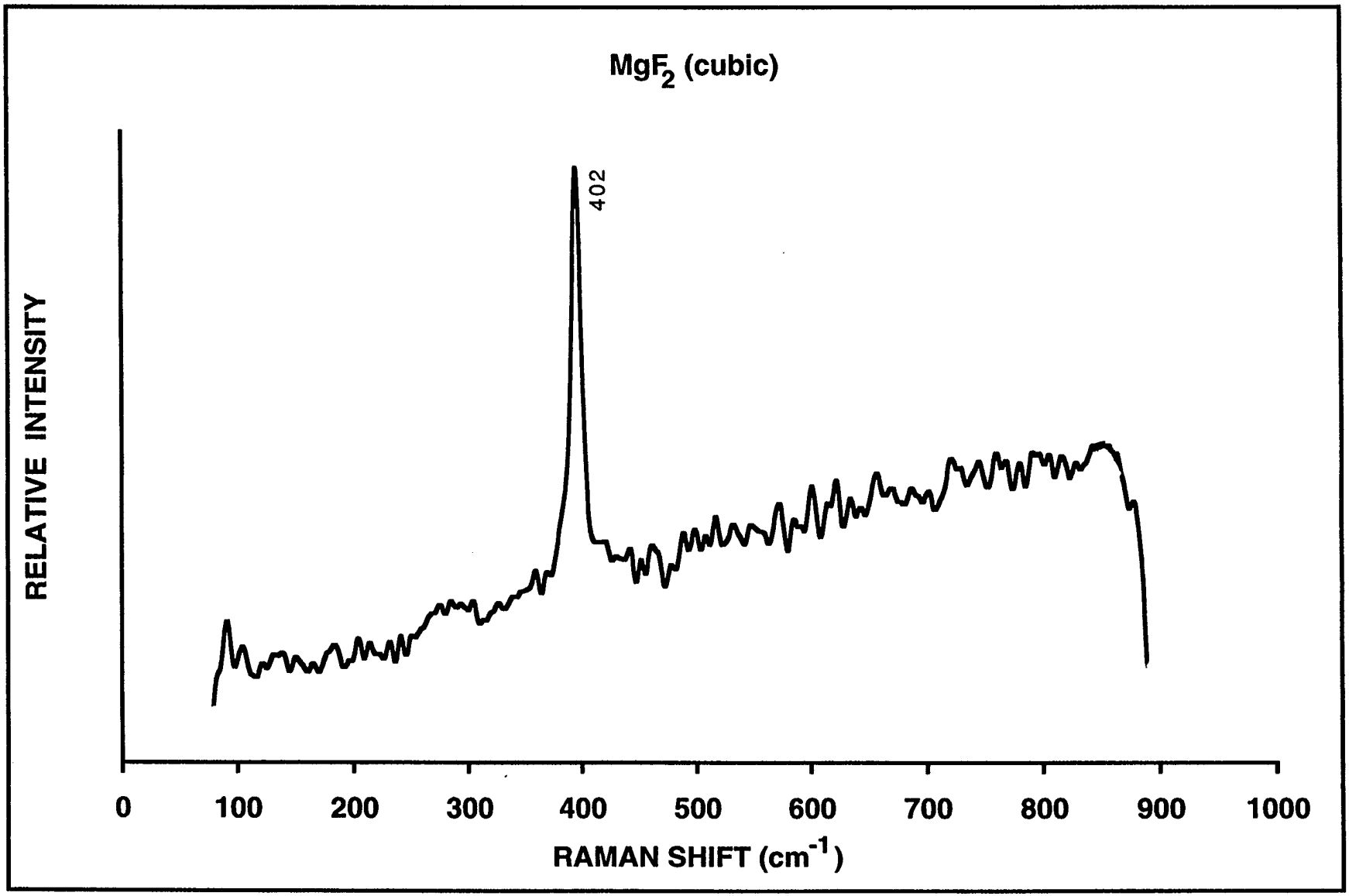

Figure A20. Raman Spectrum of MgF2.

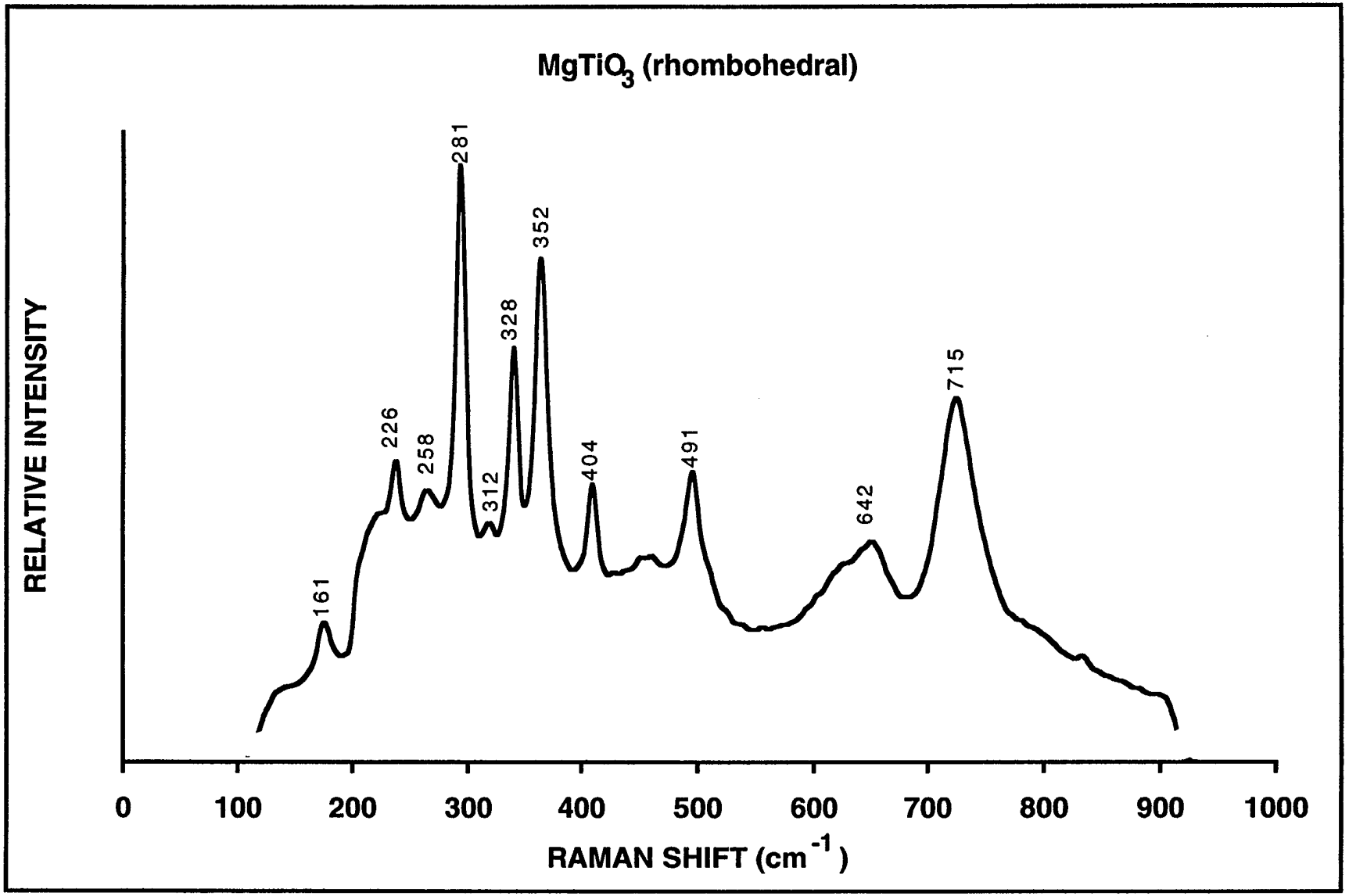

Figure A21. Raman Spectrum of MgTiO3.

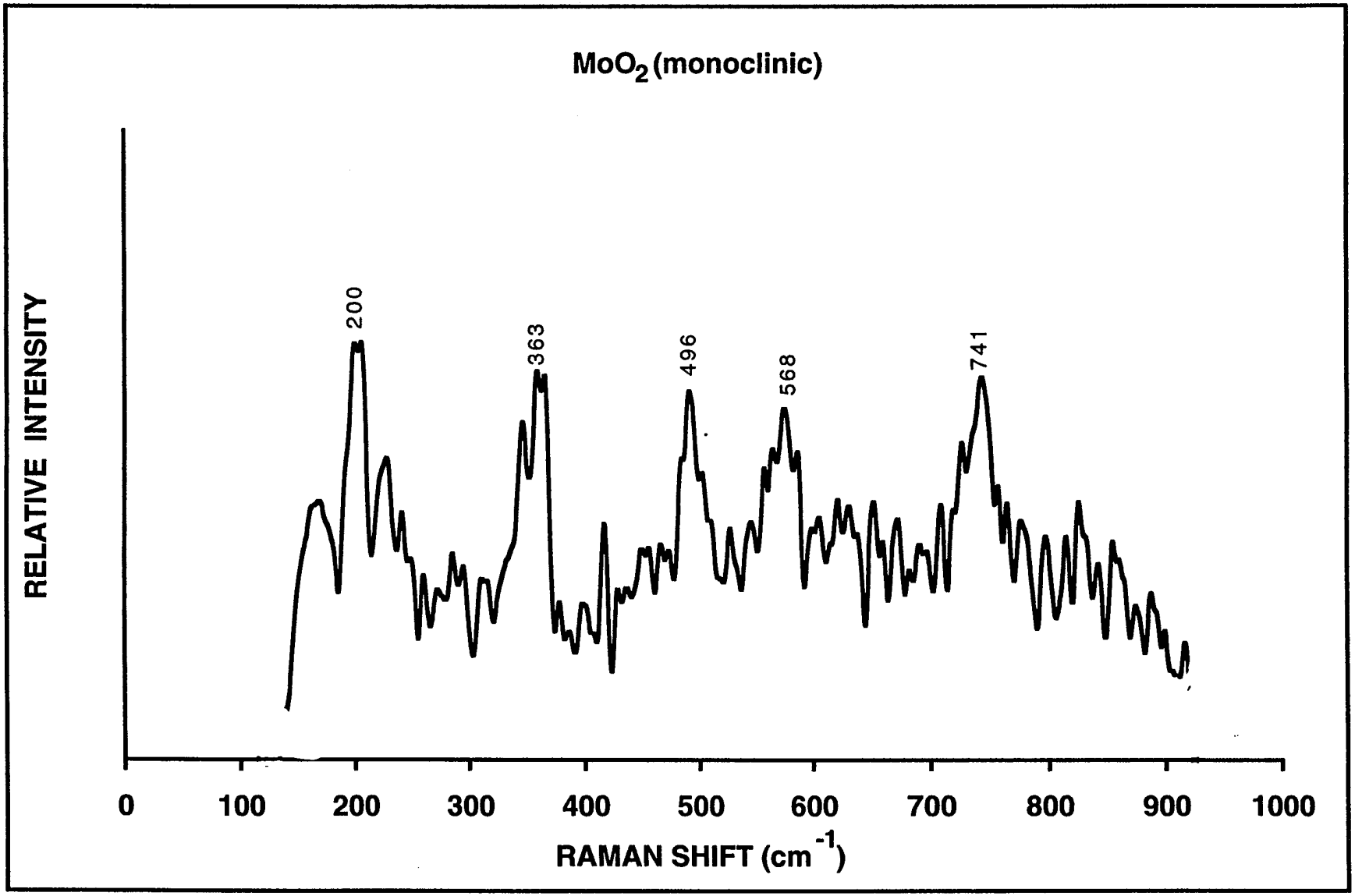

Figure A22. Raman Spectrum of MoO2.

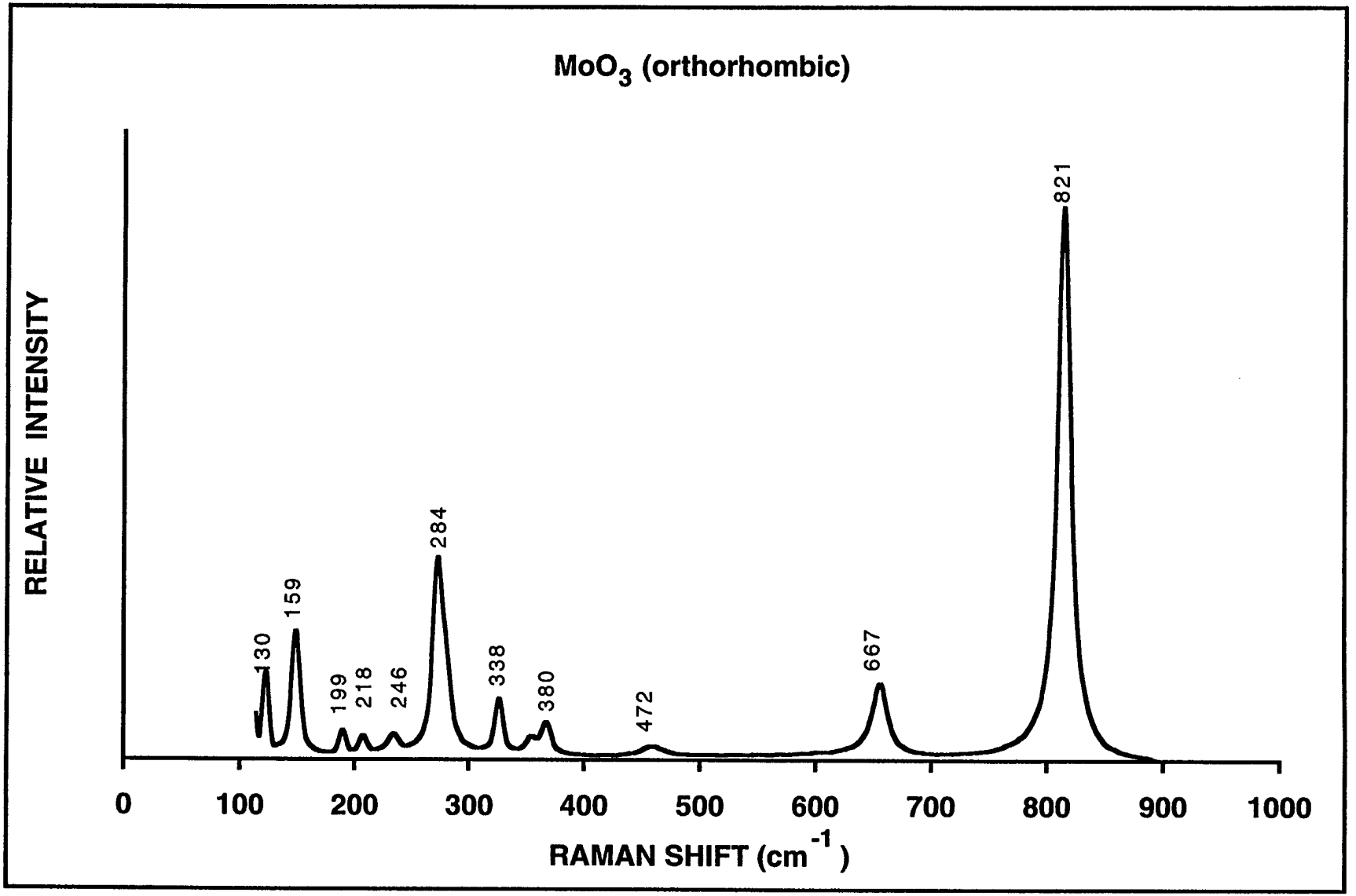

Figure A23. Raman Spectrum of MoO3.

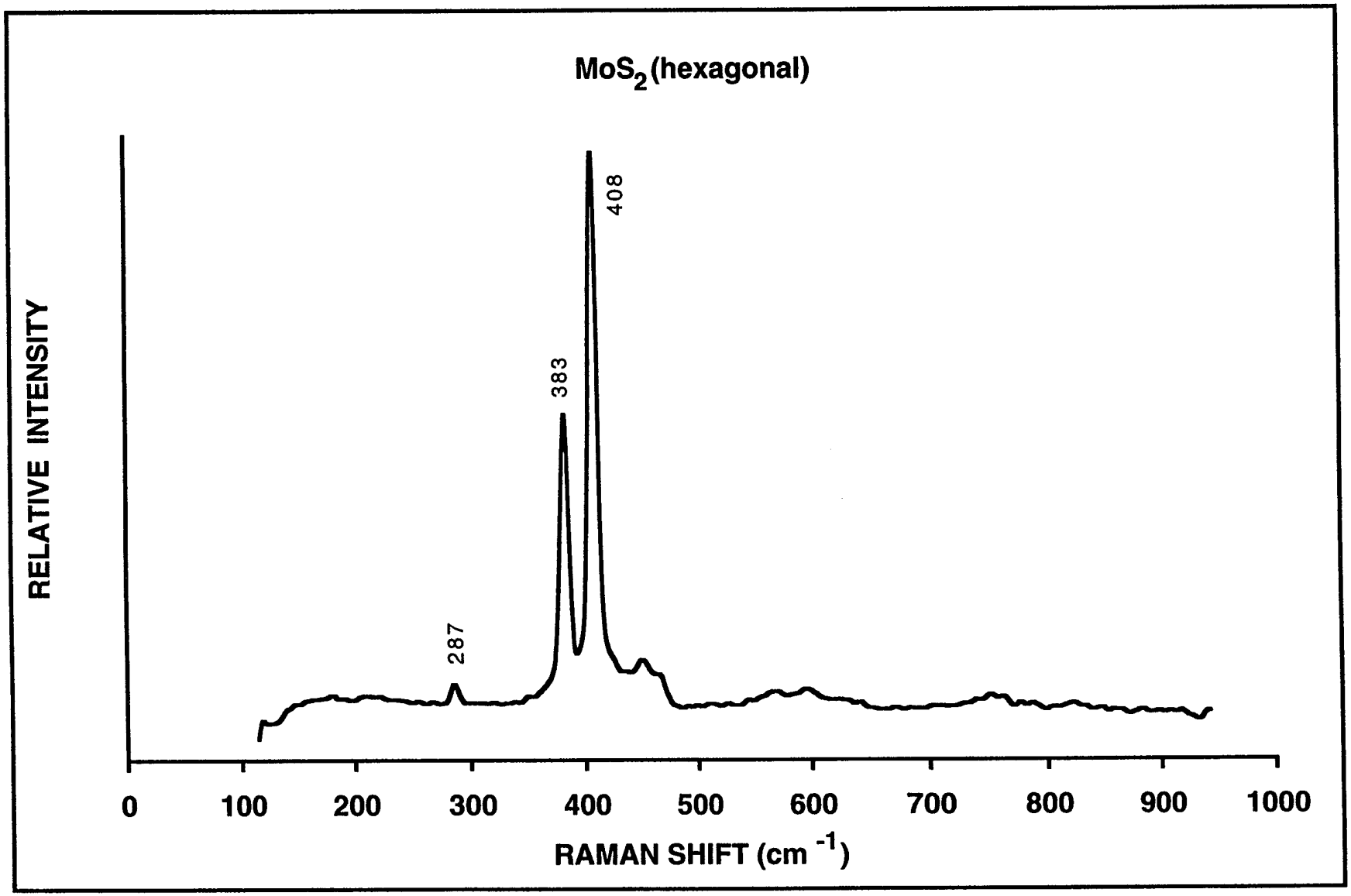

Figure A24. Raman Spectrum of MoS2 .

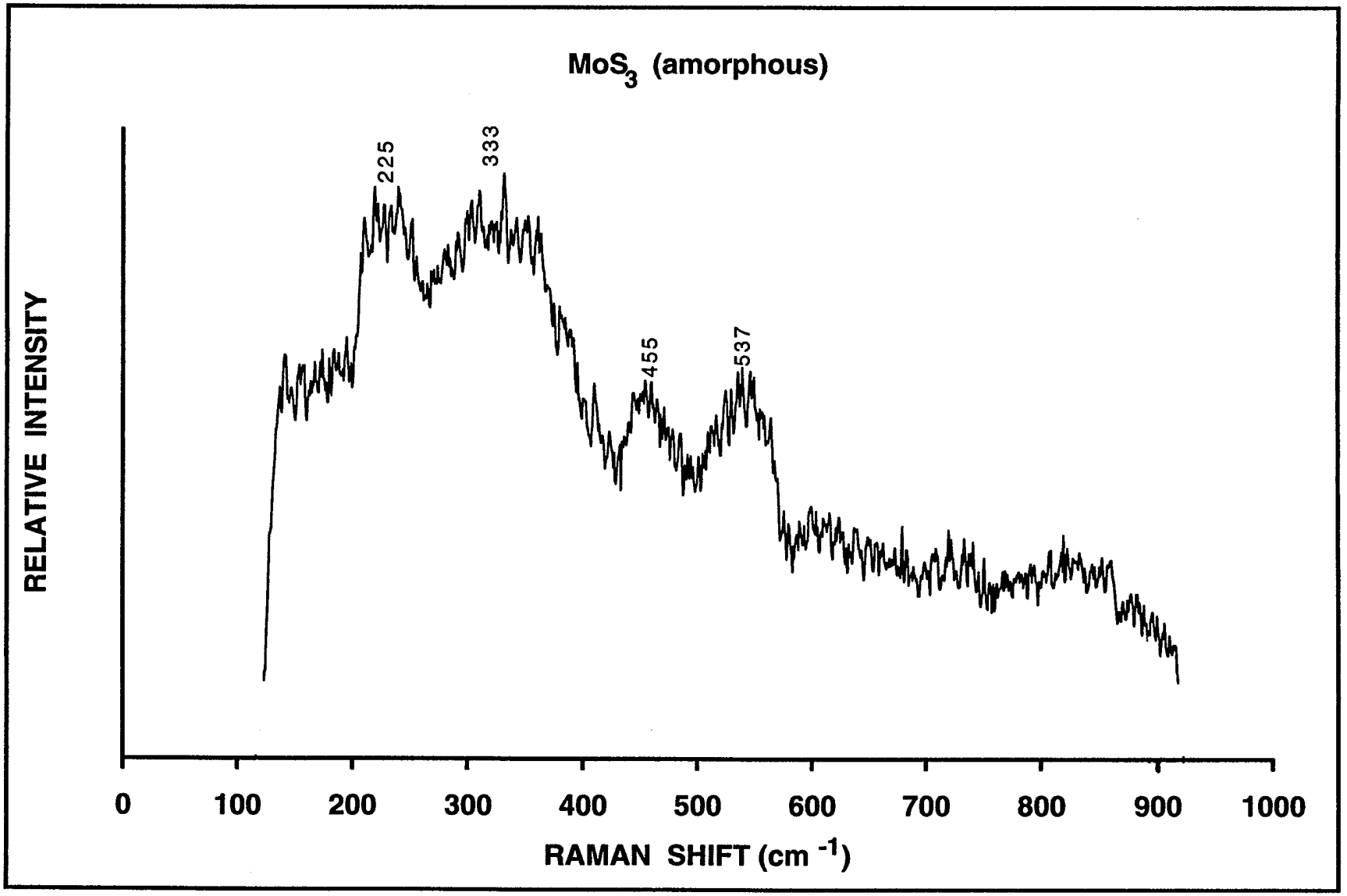

Figure A25. Raman Spectrum of MoS3.

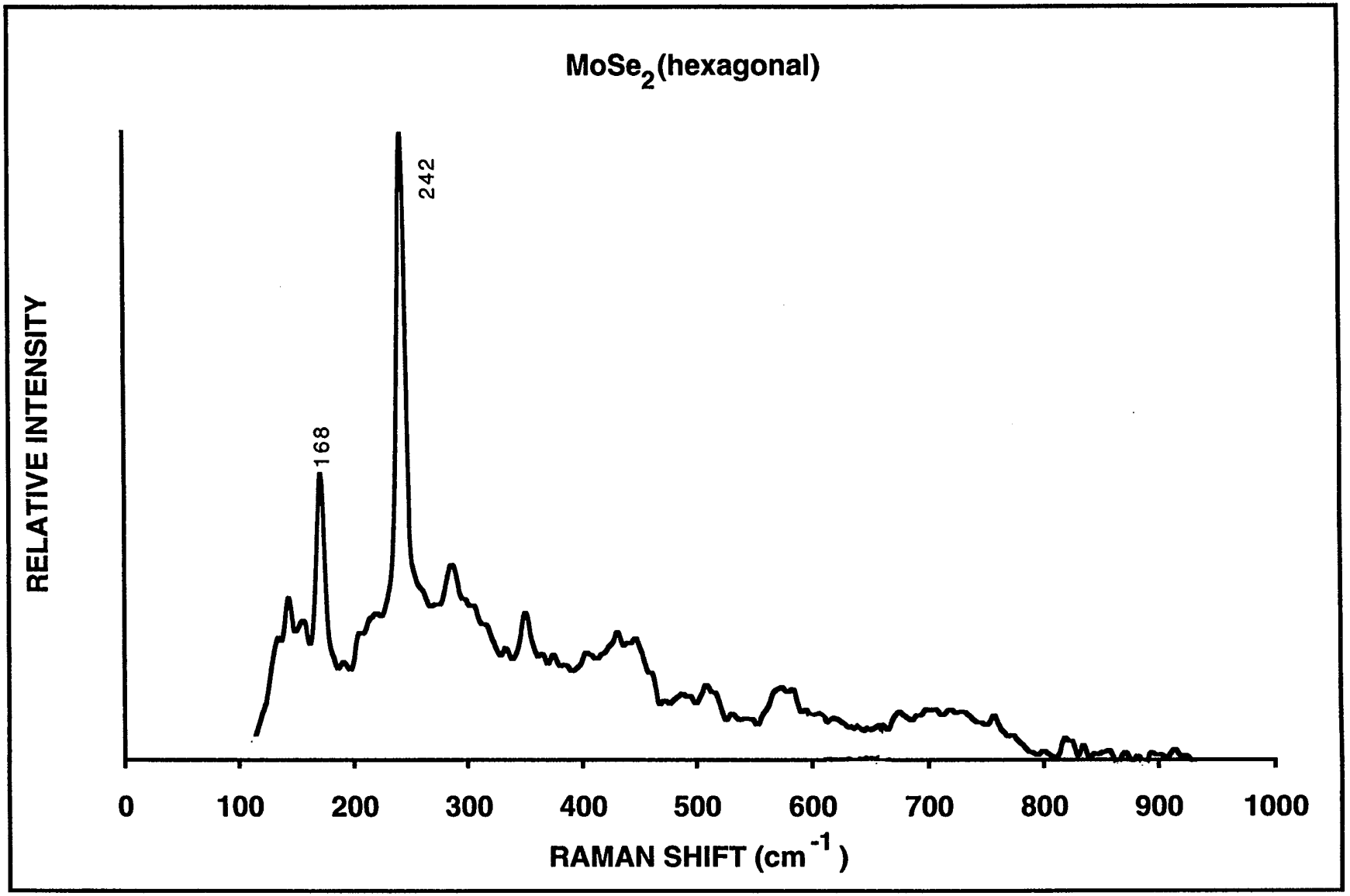

Figure A26. Raman Spectrum of MoSe2.

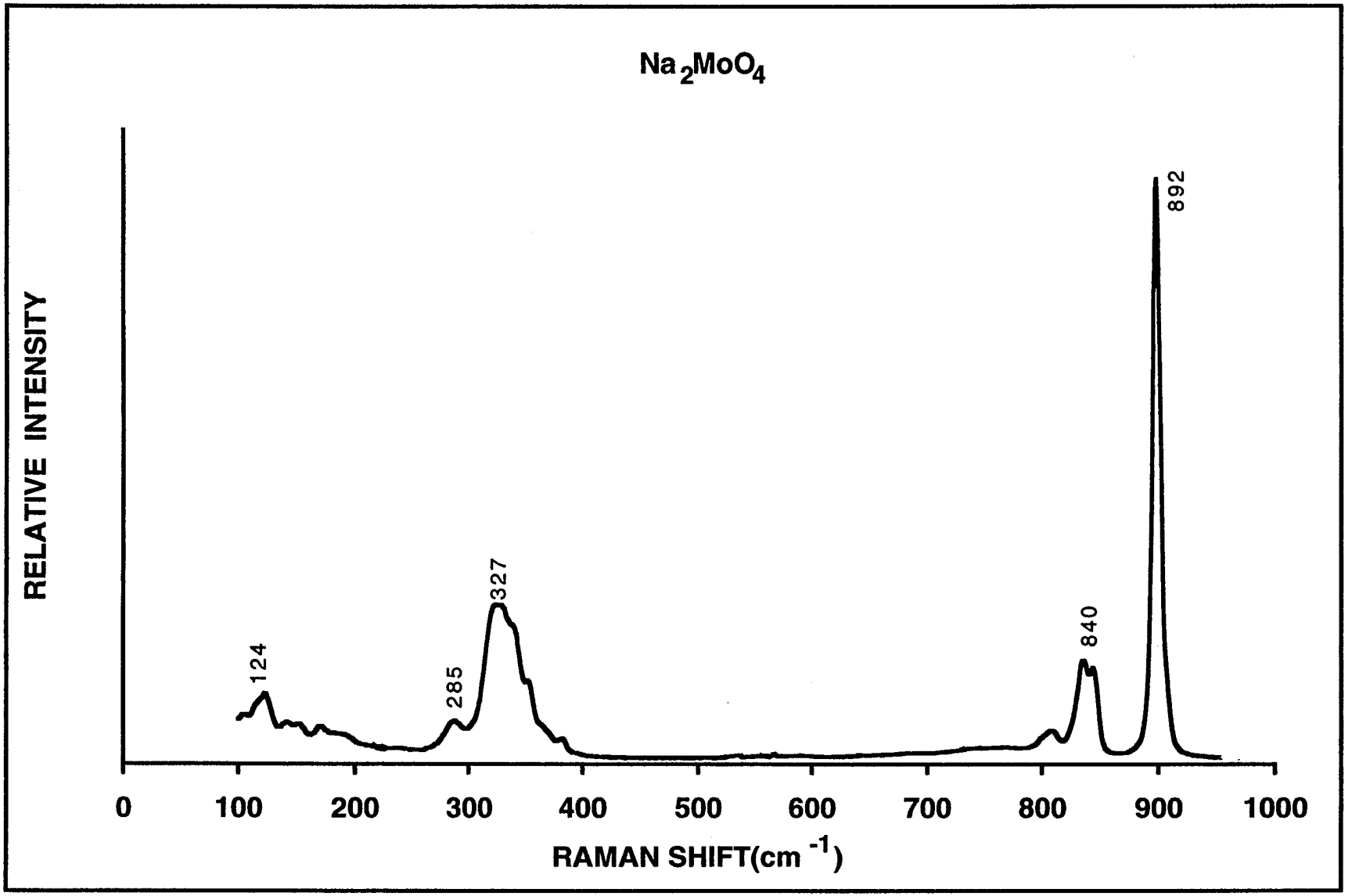

Figure A27. Raman Spectrum of Na2MoO4.

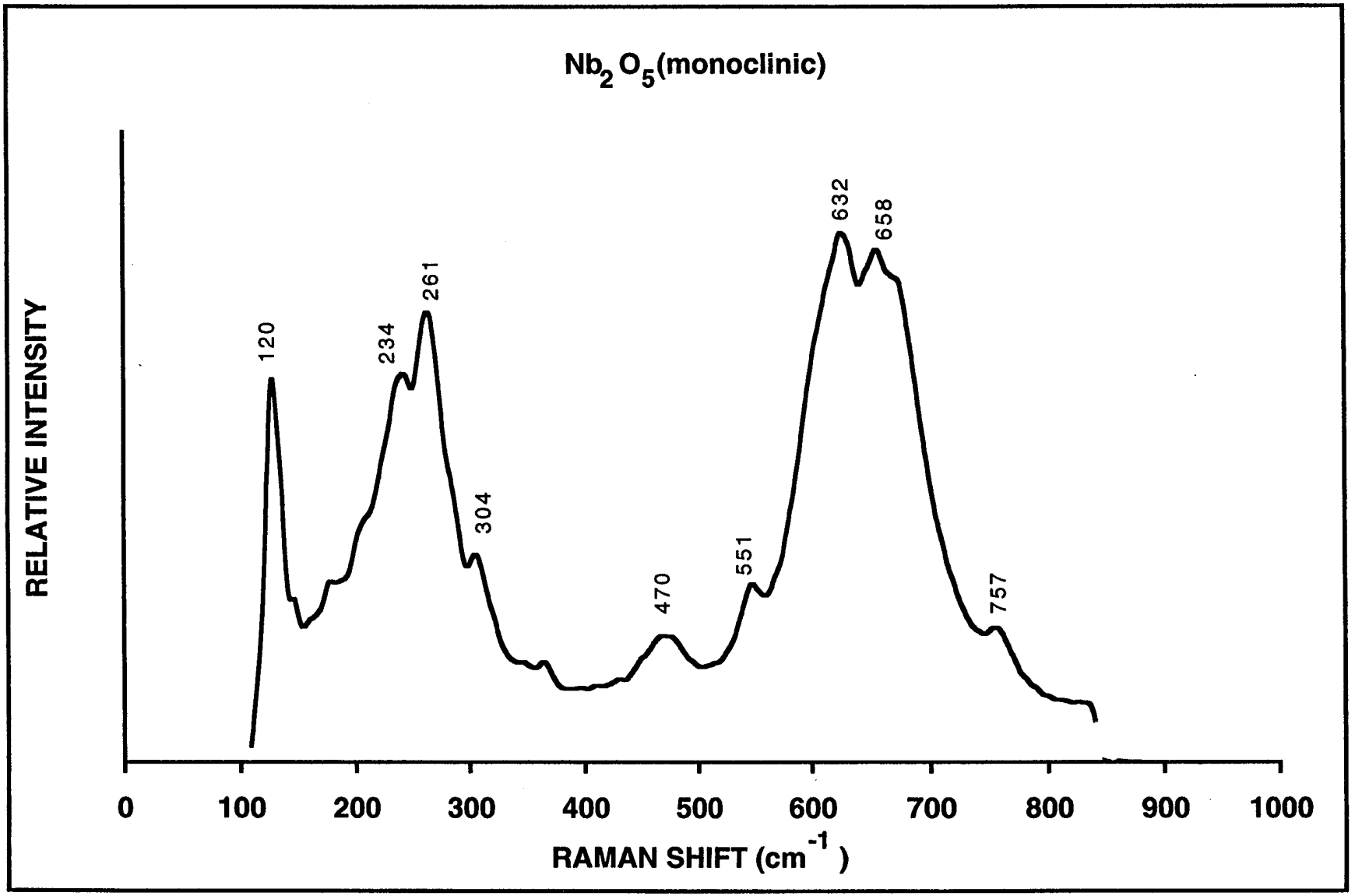

Figure A28. Raman Spectrum of Nb2O5.

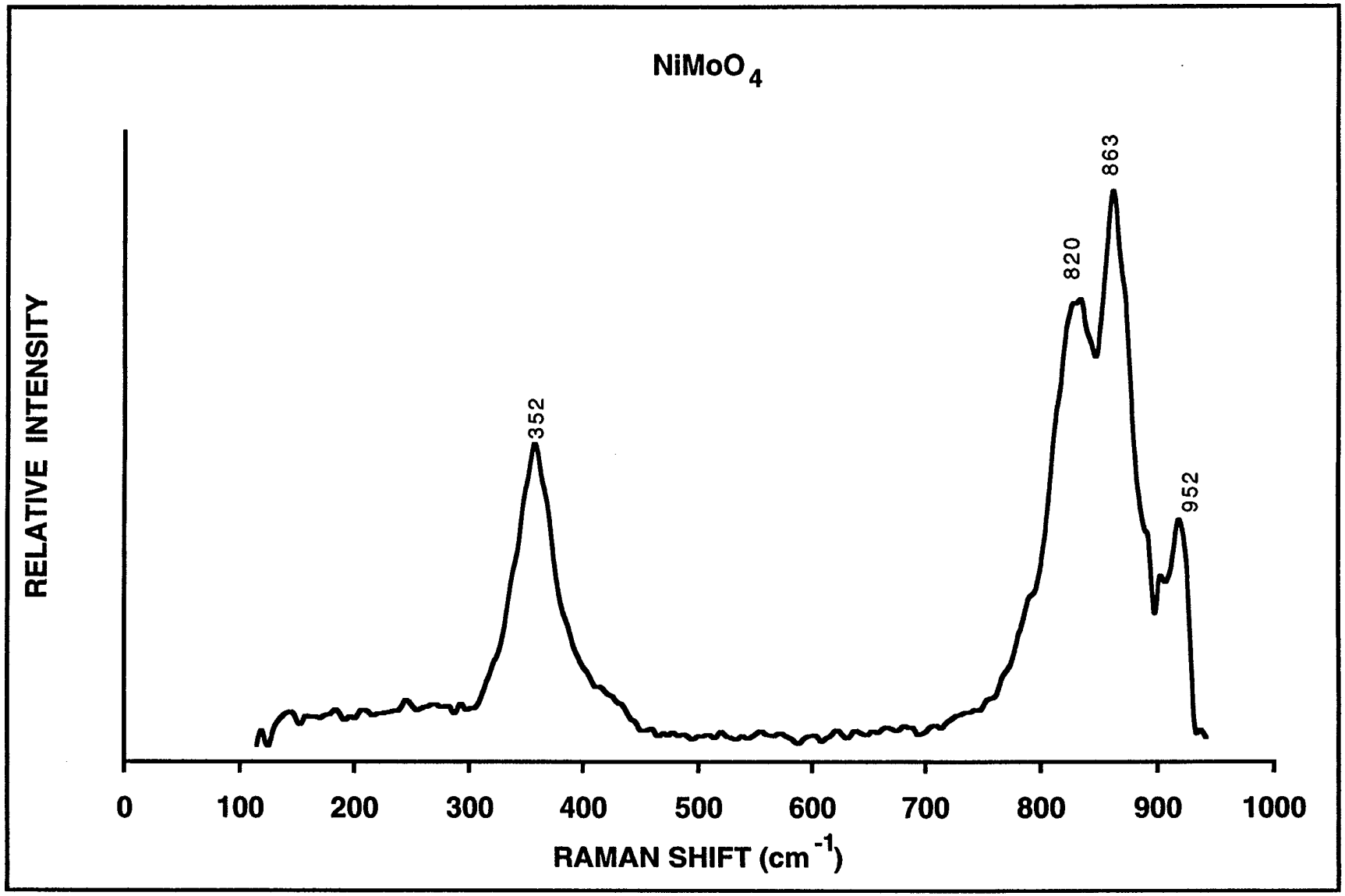

Figure A29. Raman Spectrum of NiMoO4.

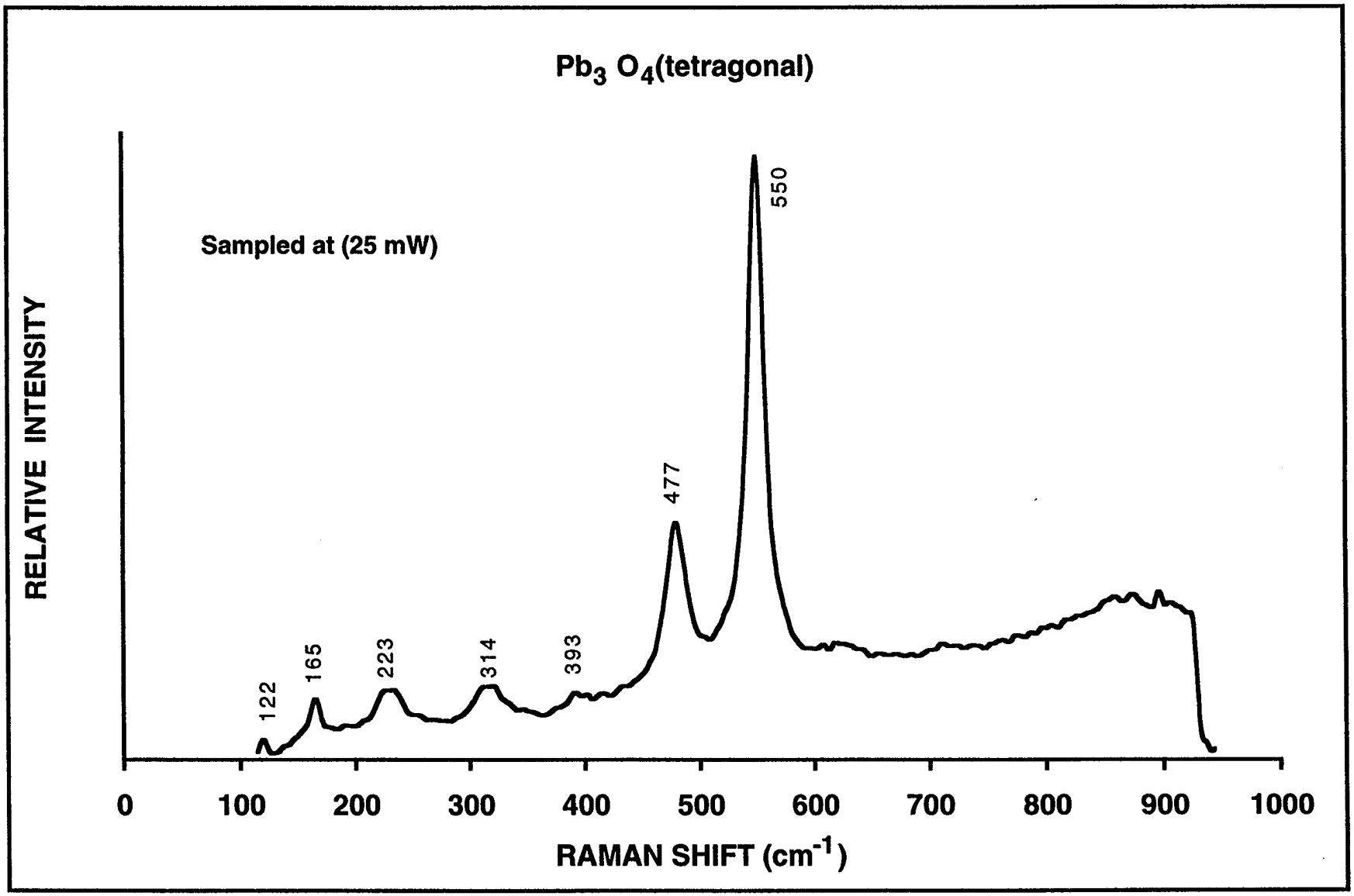

Figure A30. Raman Spectrum of Pb3O4.

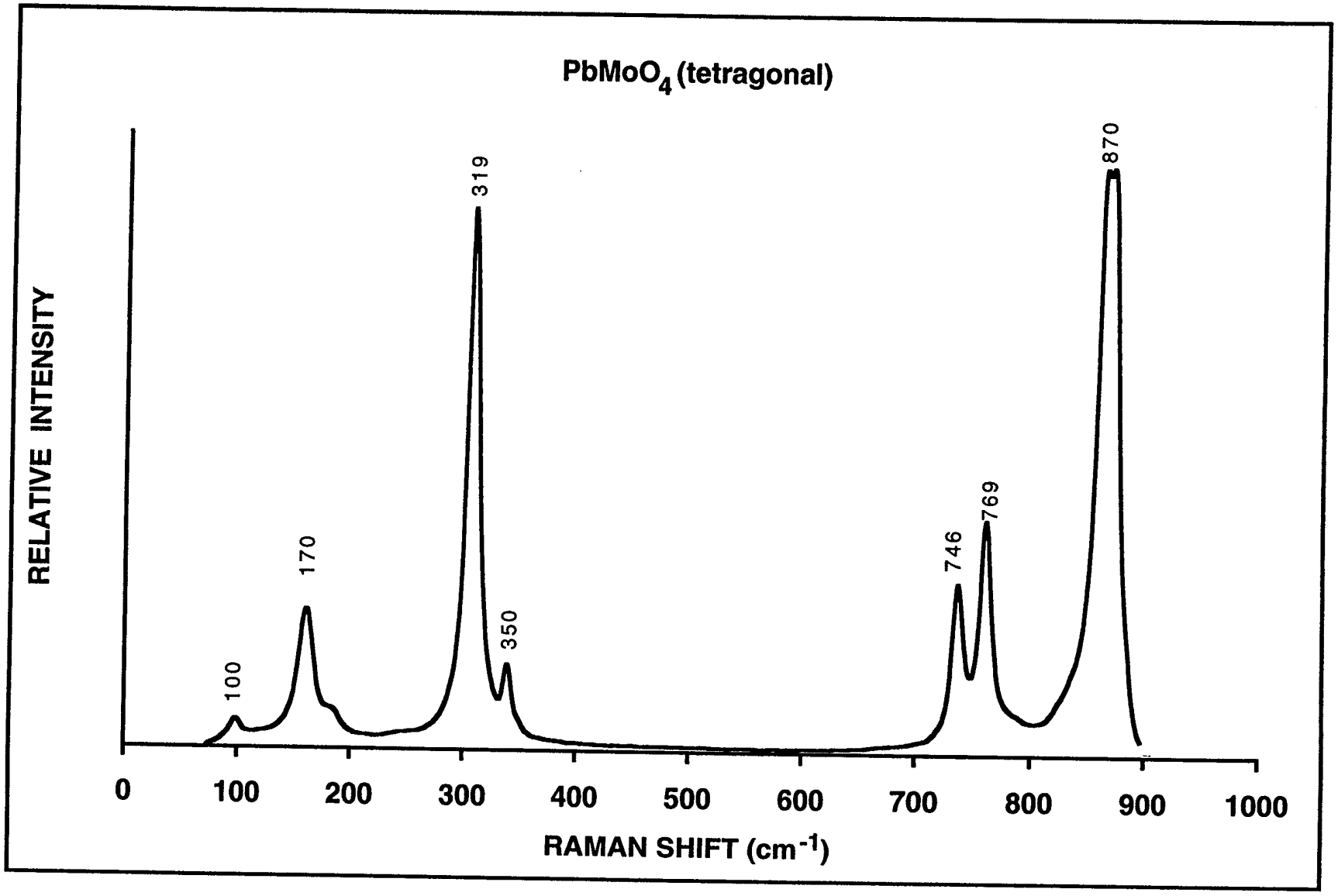

Figure A31.Raman Spectrum of PbMoO4.

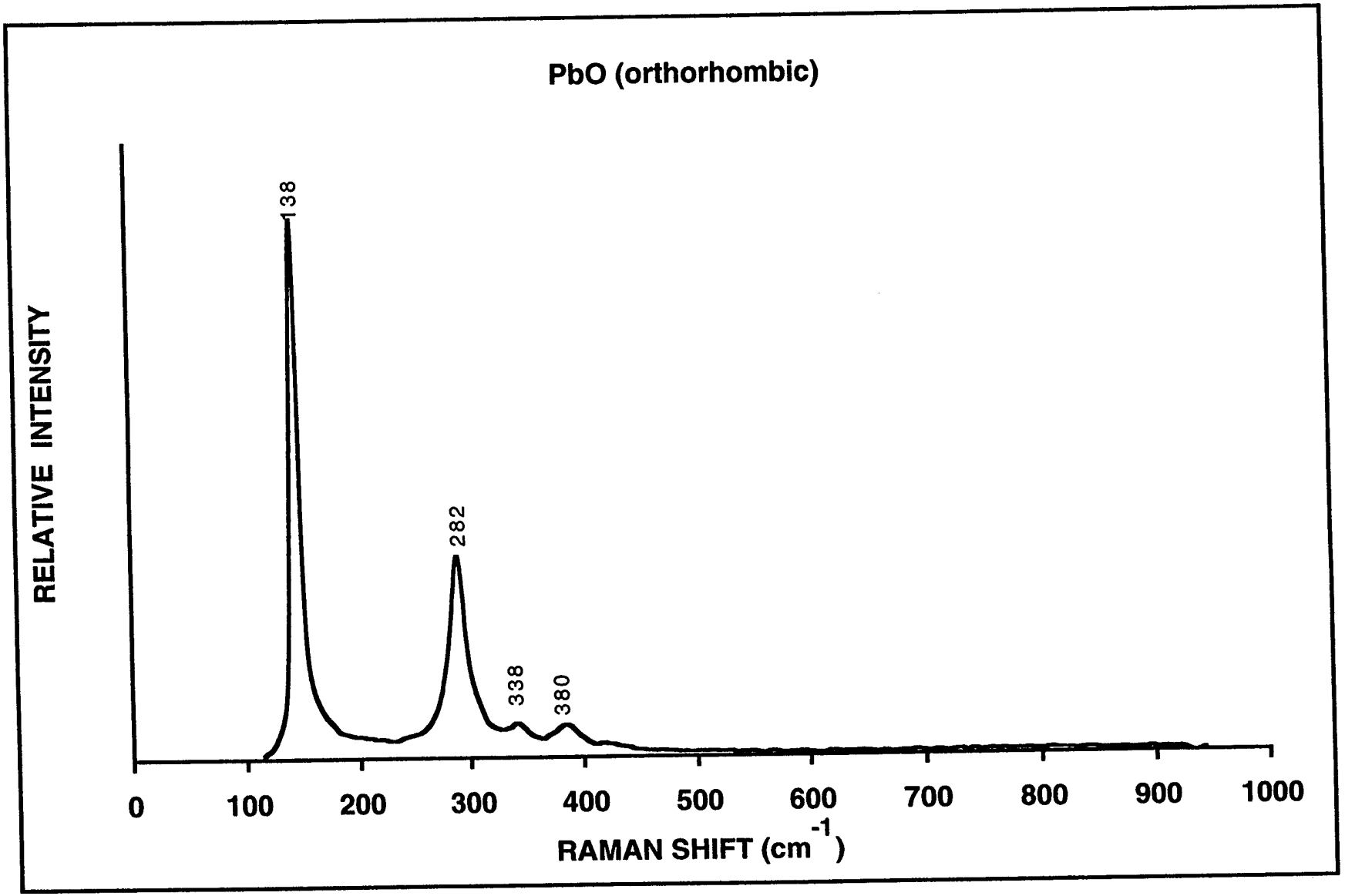

Figure A32. Raman Spectrum of PbO.

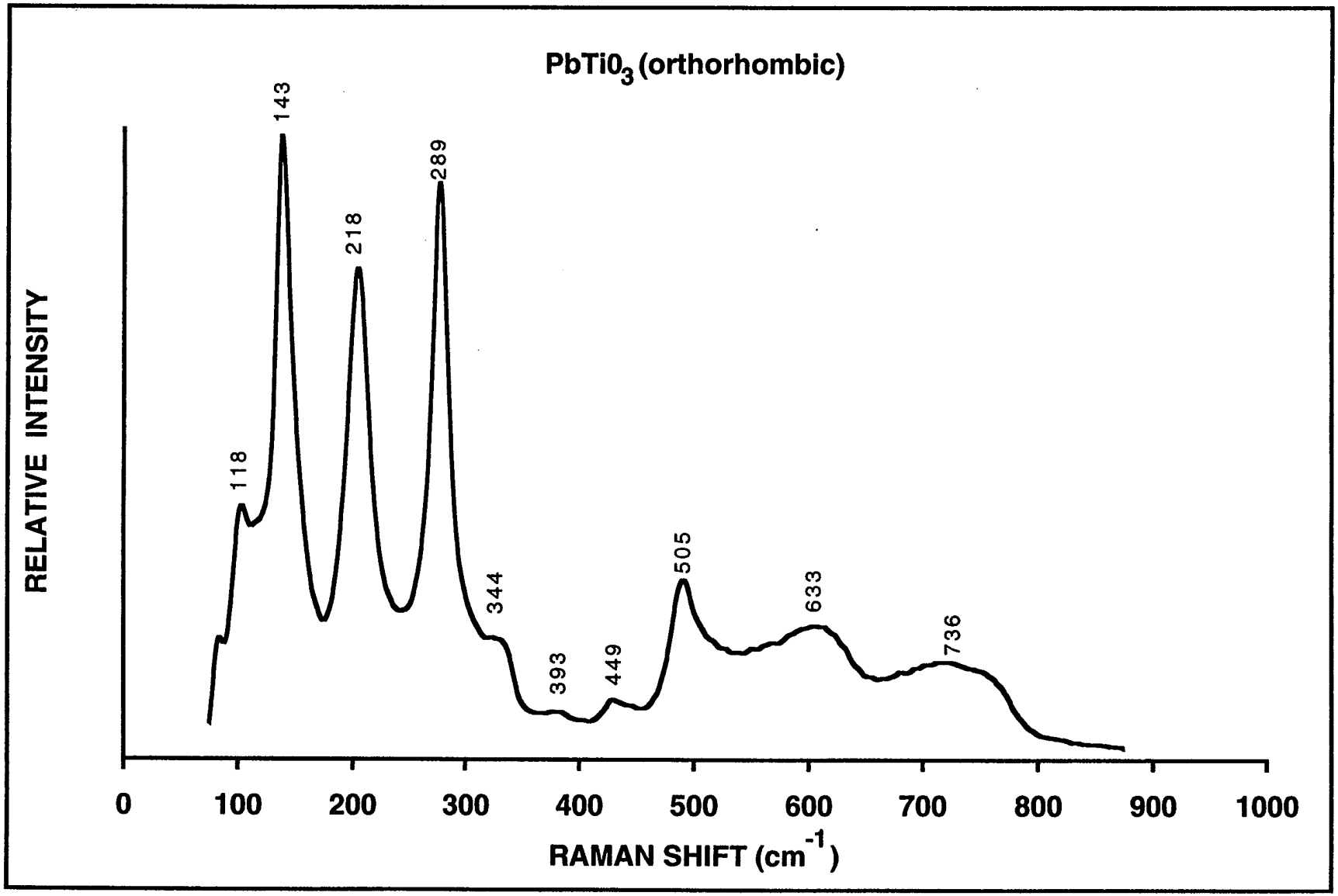

Figure A33. Raman Spectrum of PbTiO3.

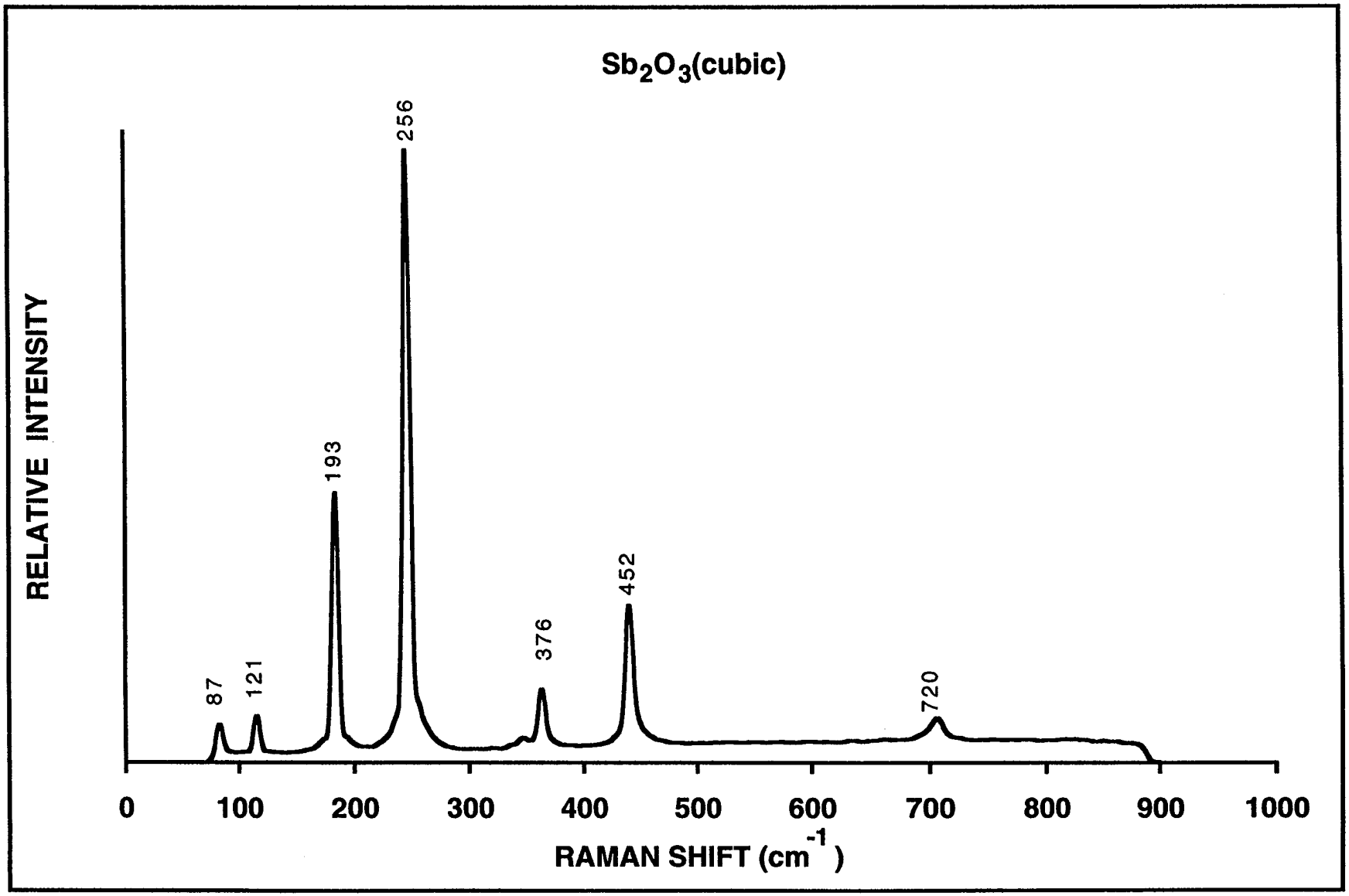

Figure A34. Raman Spectrum of Sb2O3.

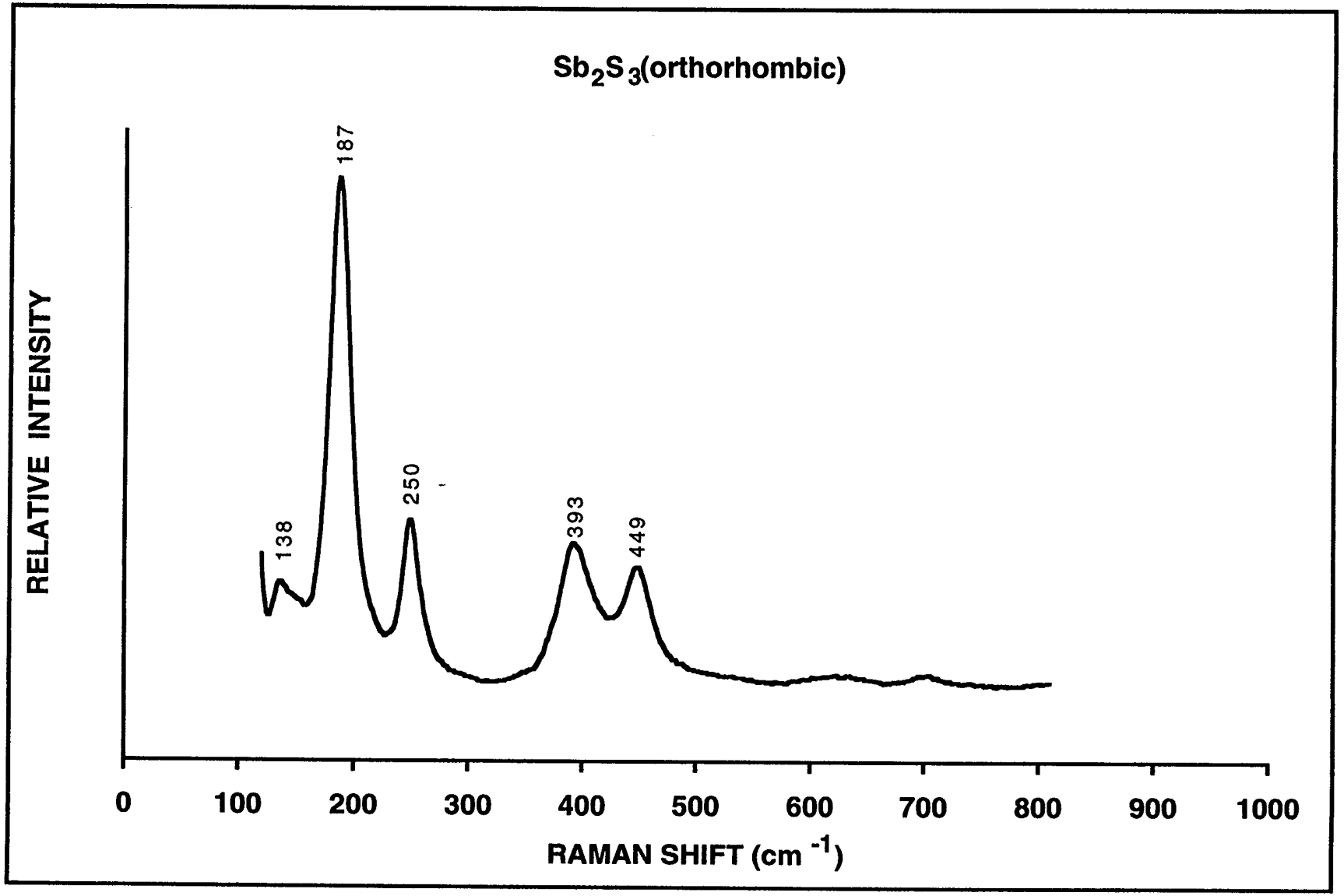

Figure A35. Raman Spectrum of Sb2S3.

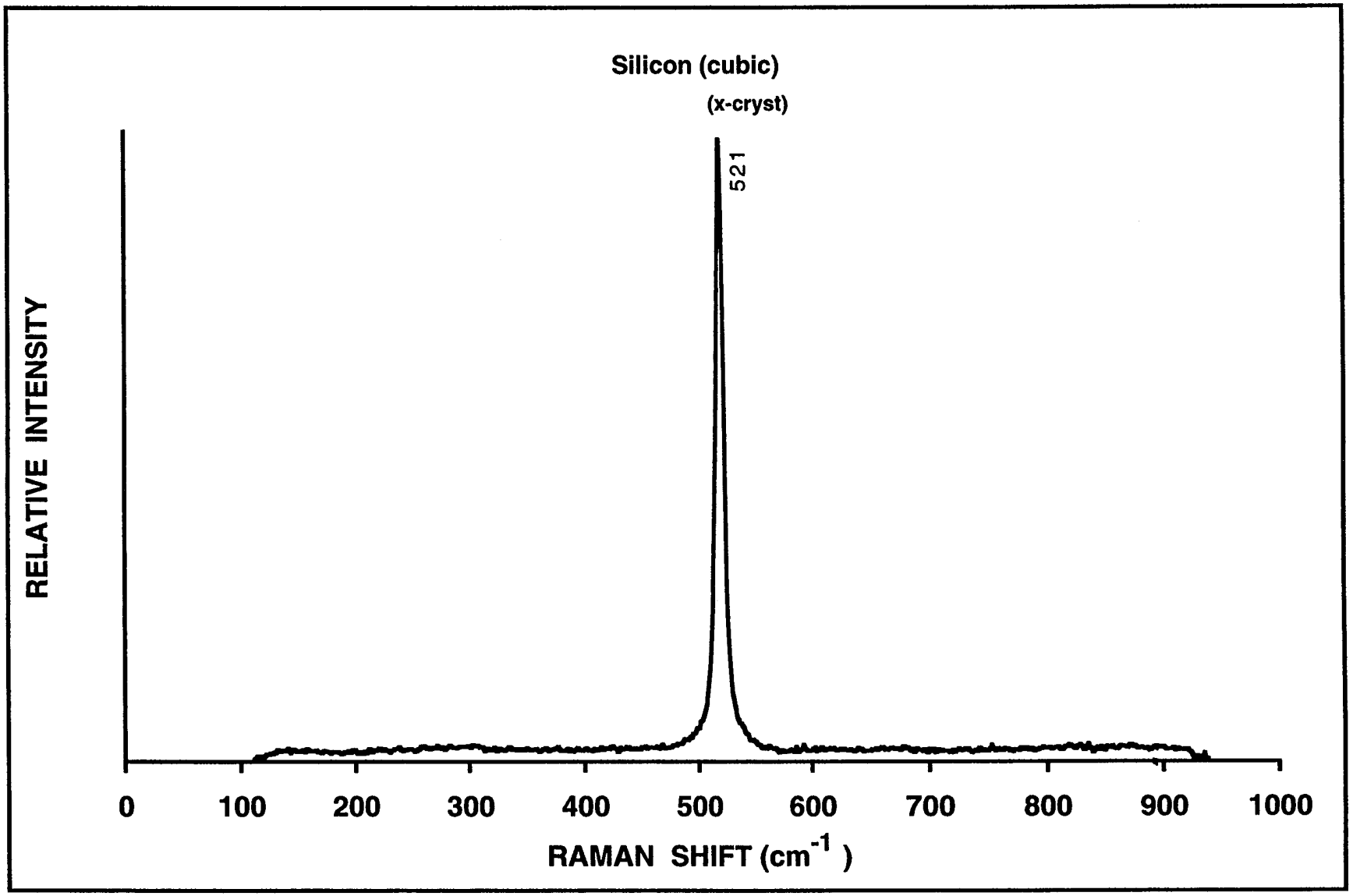

Figure A36. Raman Spectrum of Silicon.

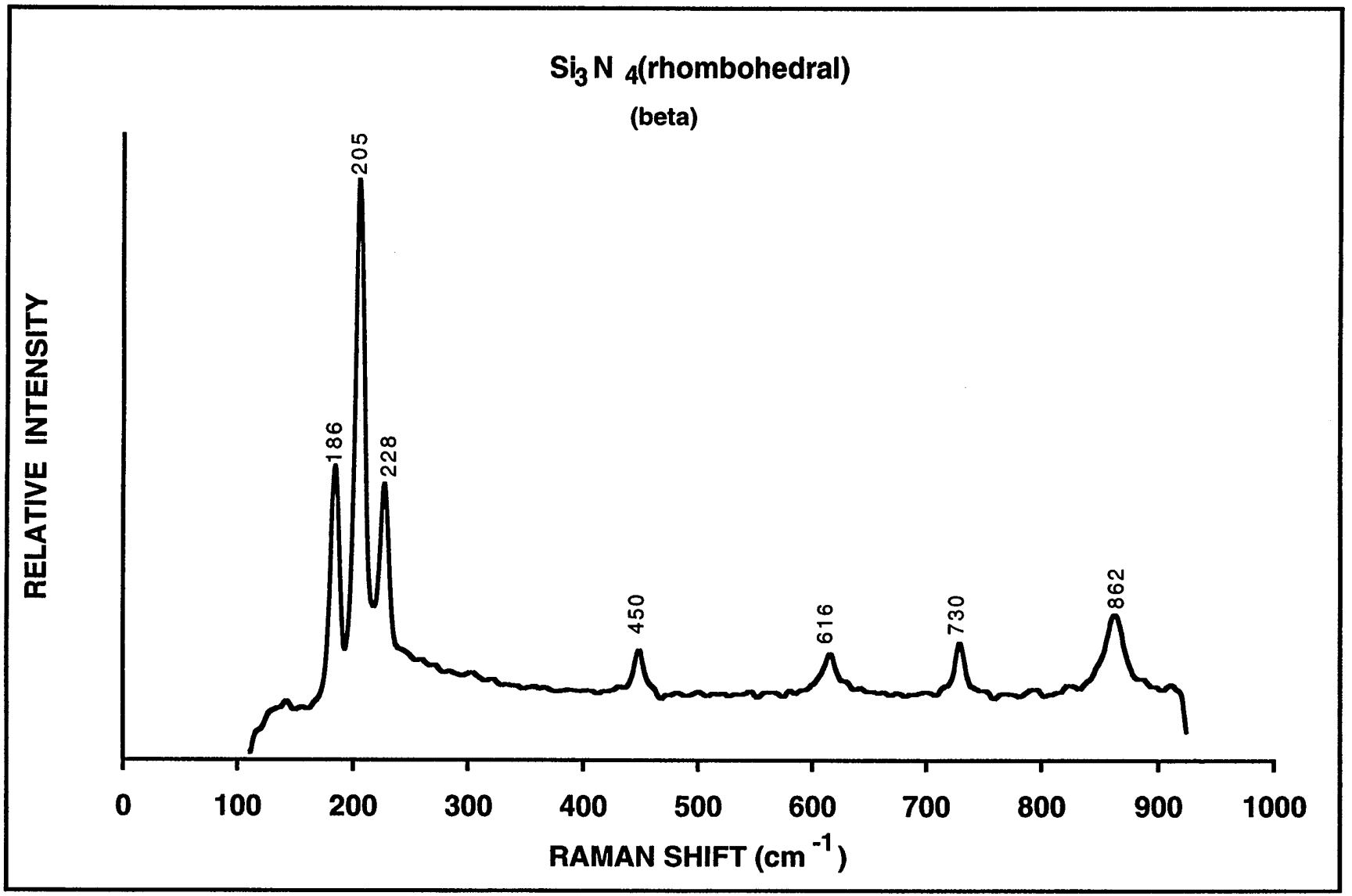

Figure A37. Raman Spectrum of Si3N4.

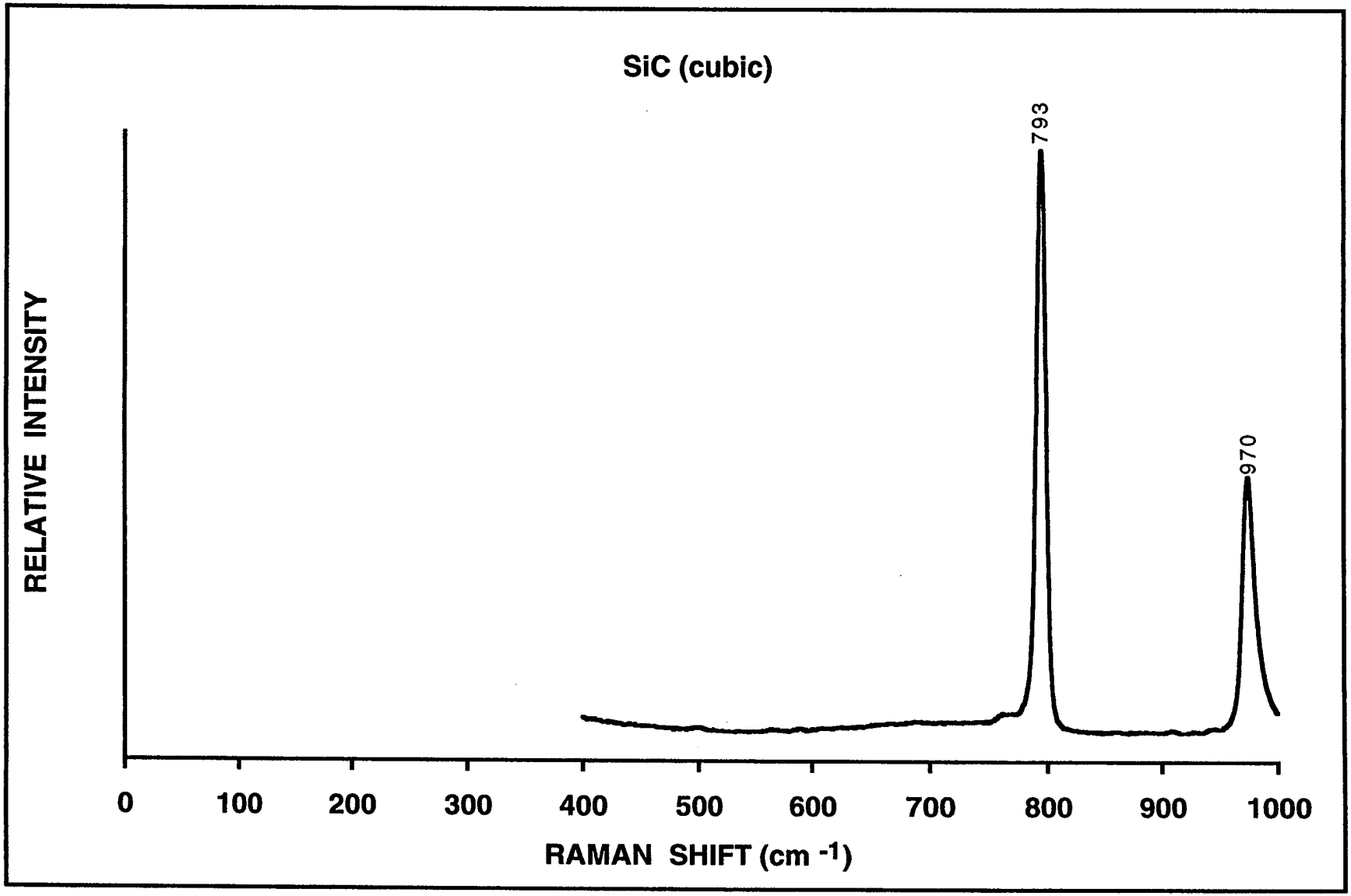

Figure A38. Raman Spectrum of SiC.

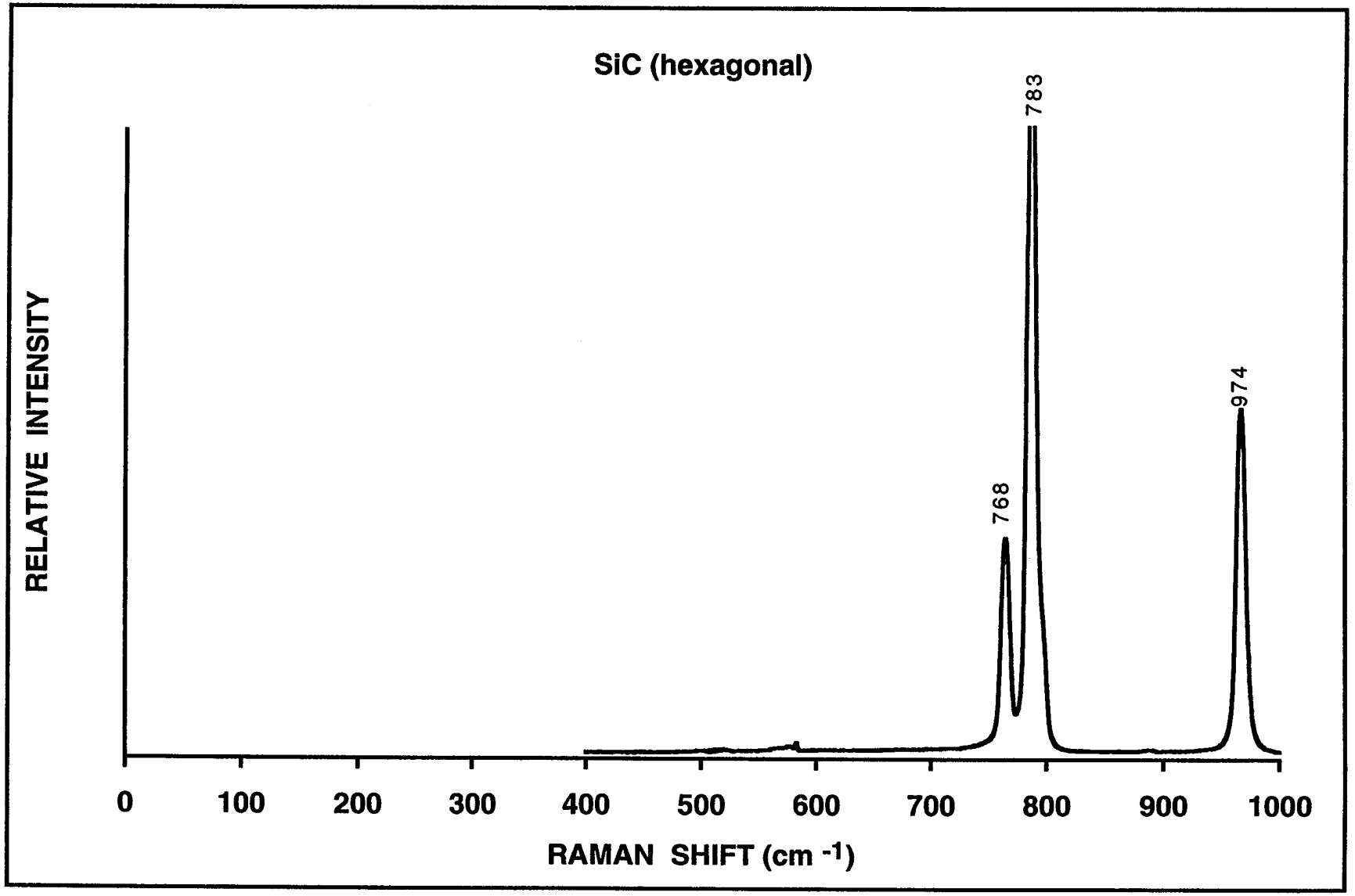

Figure A39. Raman Spectrum of SiC.

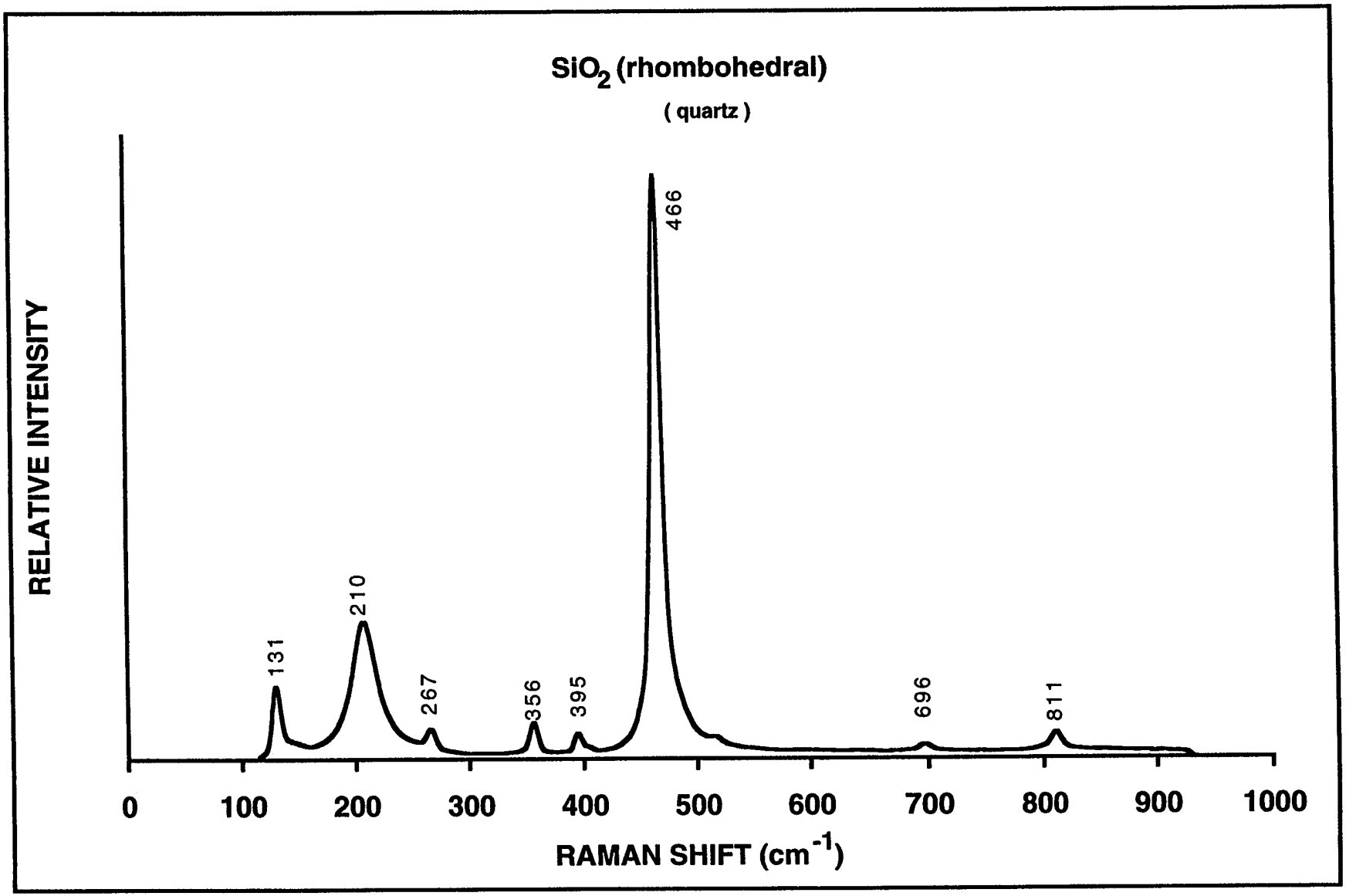

Figure A40. Raman Spectrum of SiO2.

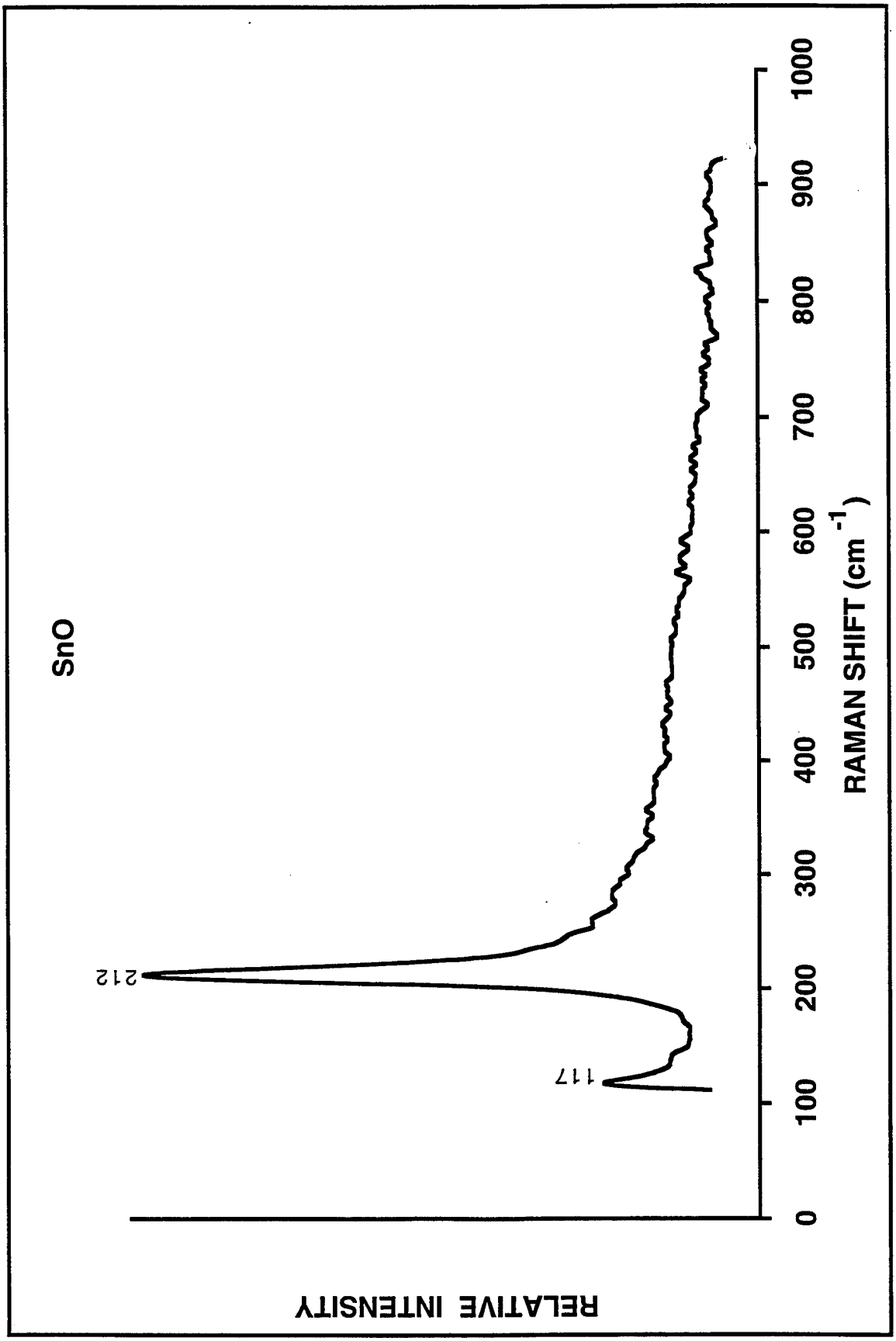

Figure A41. Raman Spectrum of SnO.

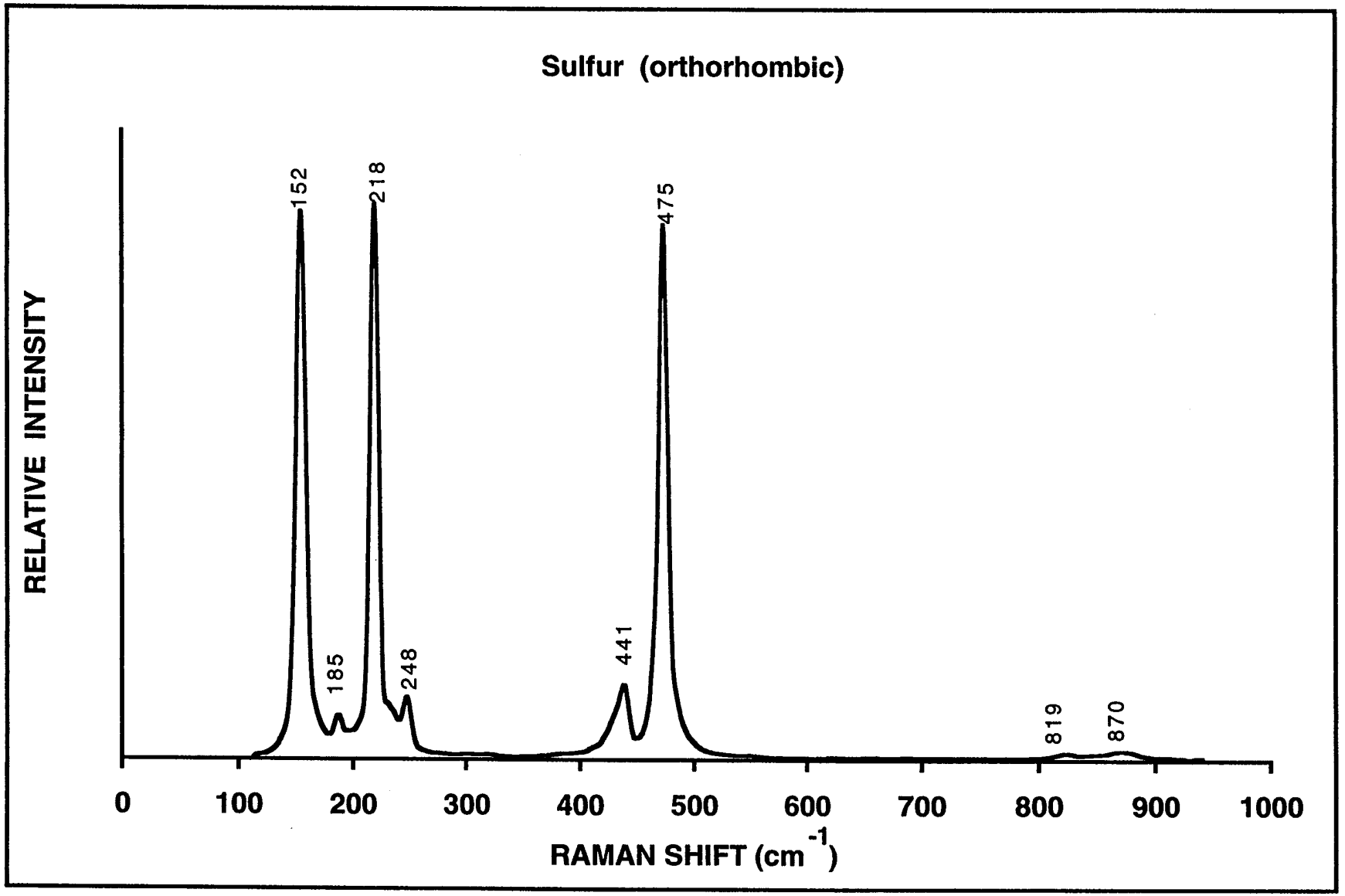

Figure A42. Raman Spectrum of Sulfur.

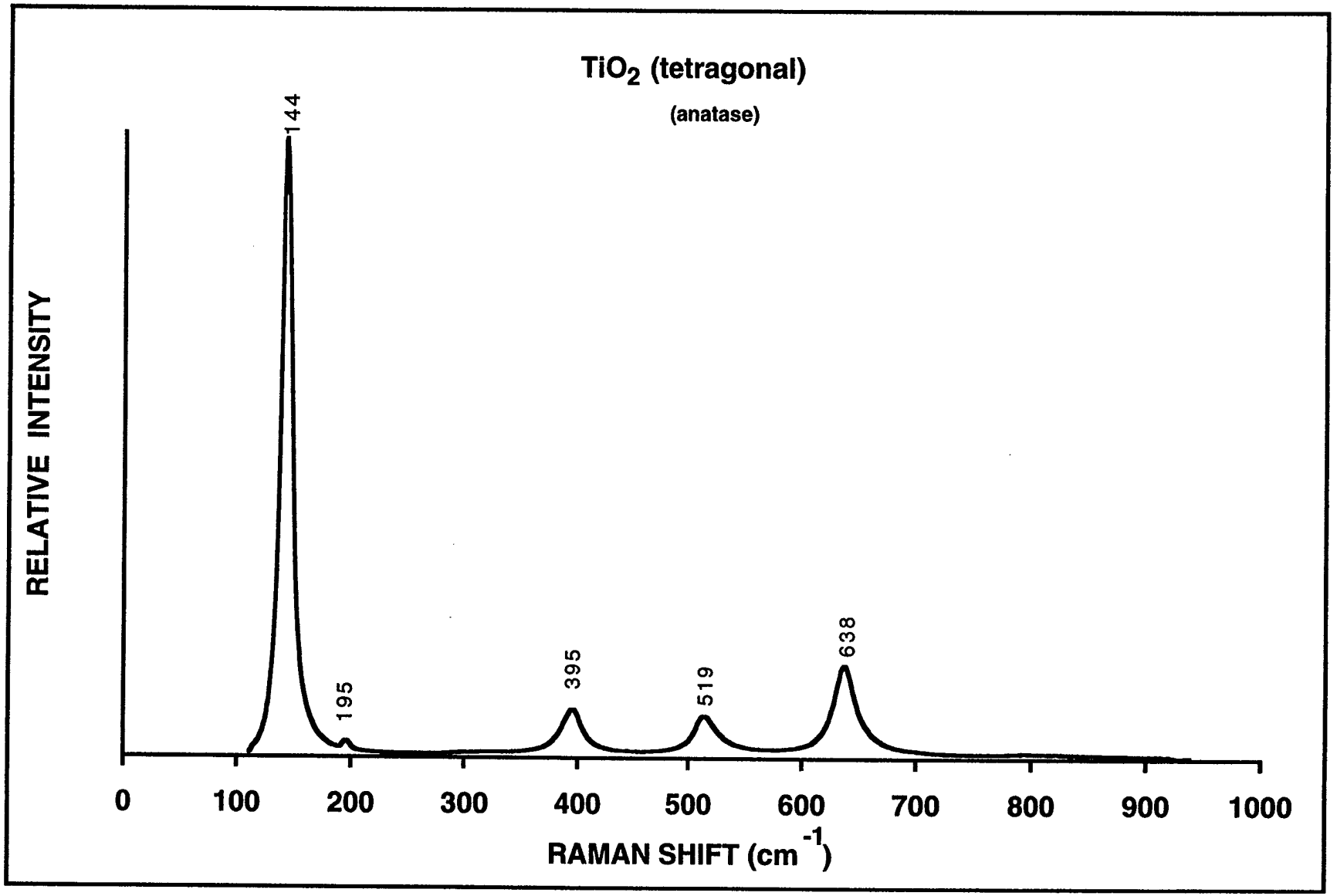

Figure A43. Raman Spectrum of TiO2.

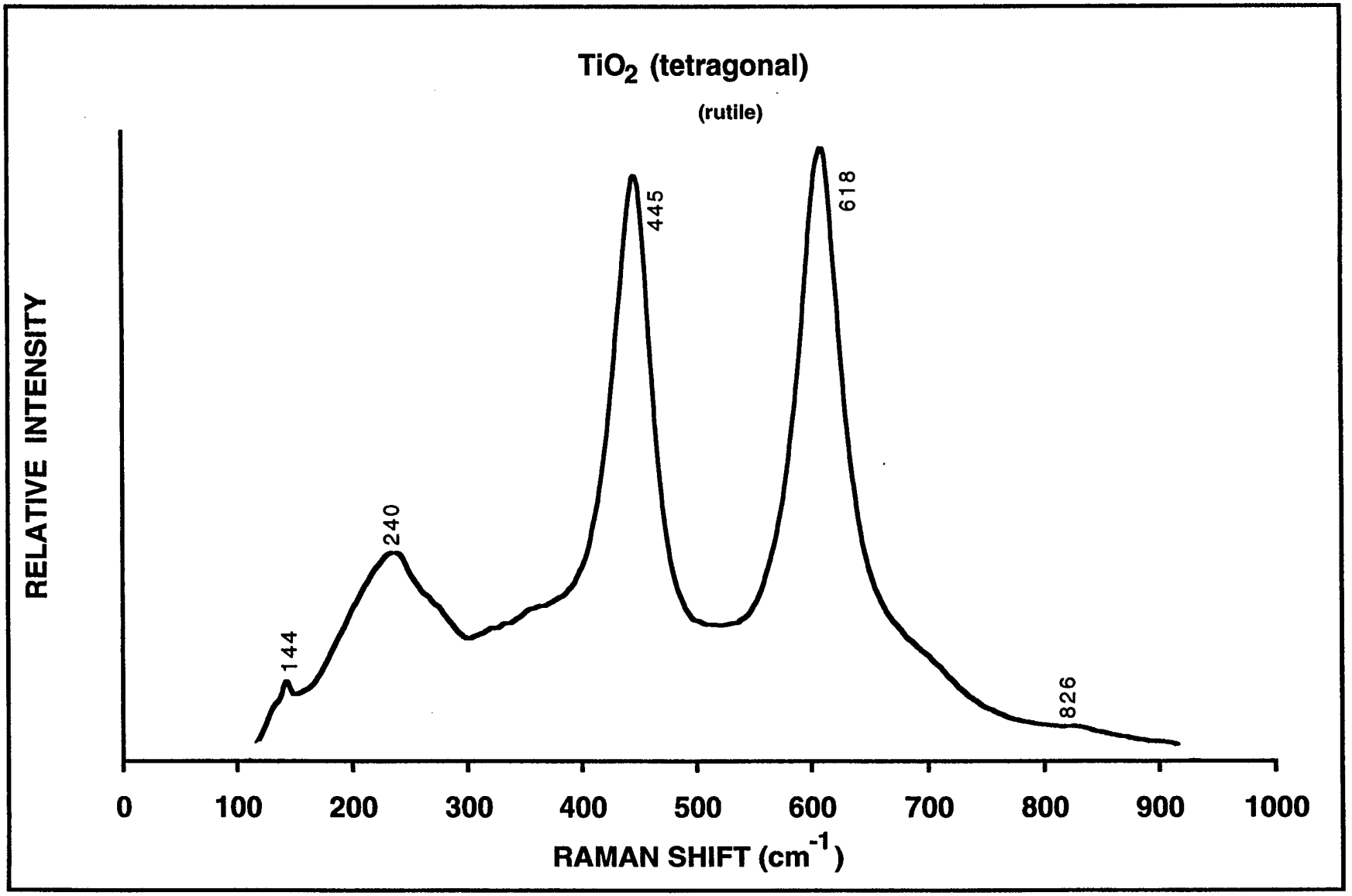

Figure A44. Raman Spectrum of TiO2.

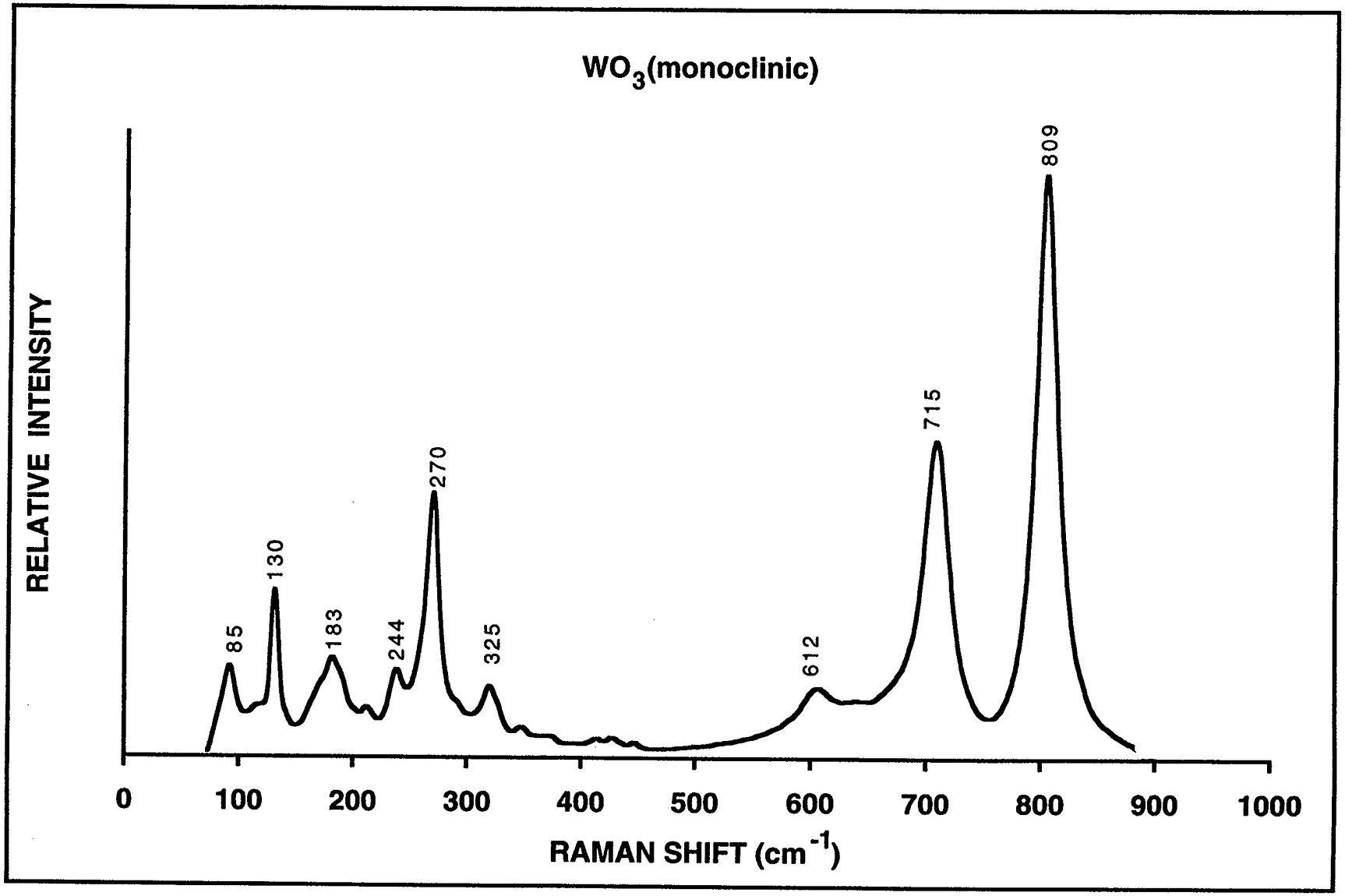

Figure A45. Raman Spectrum of WO3.

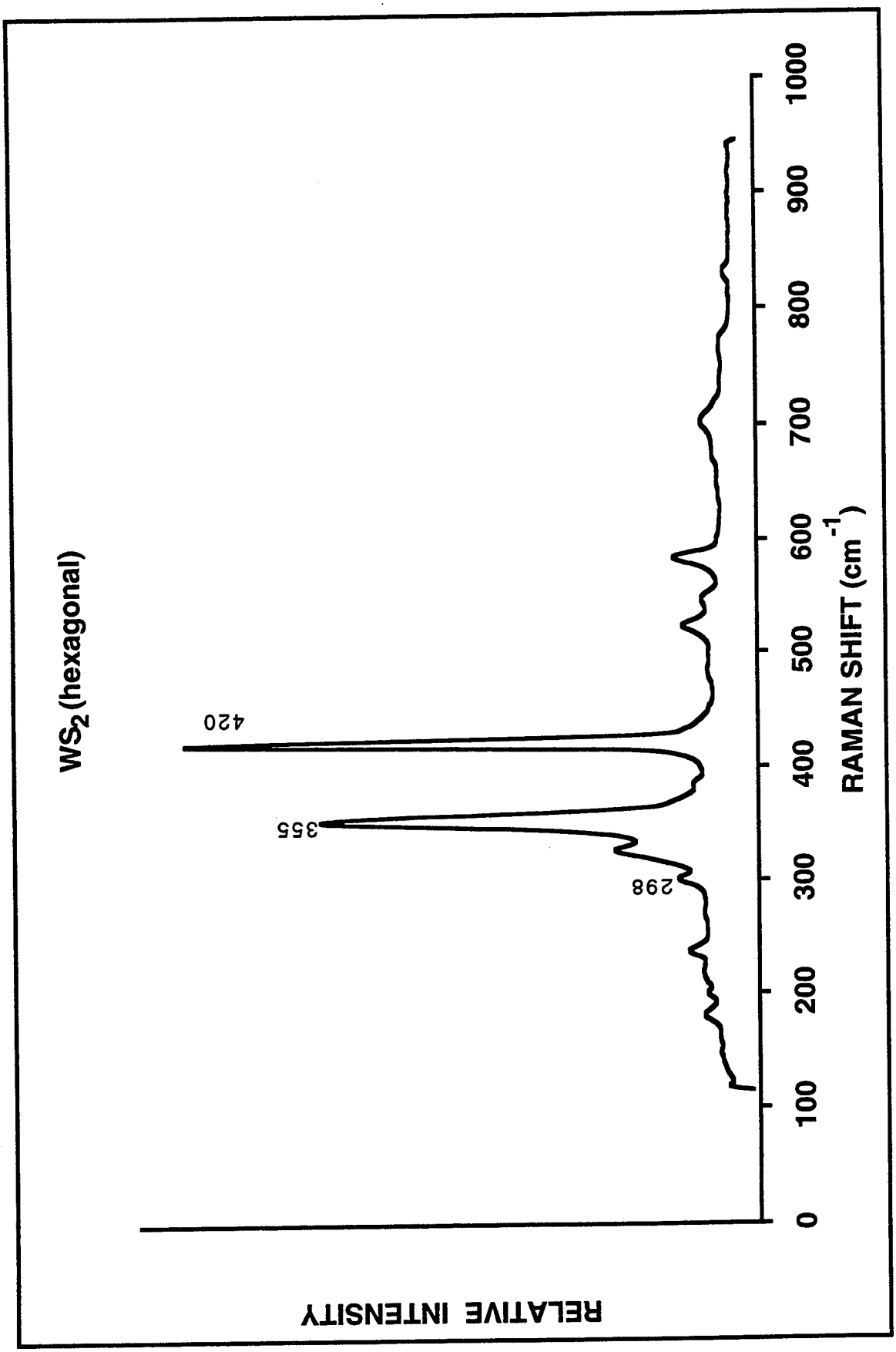

Figure A46. Raman Spectrum of WS2.

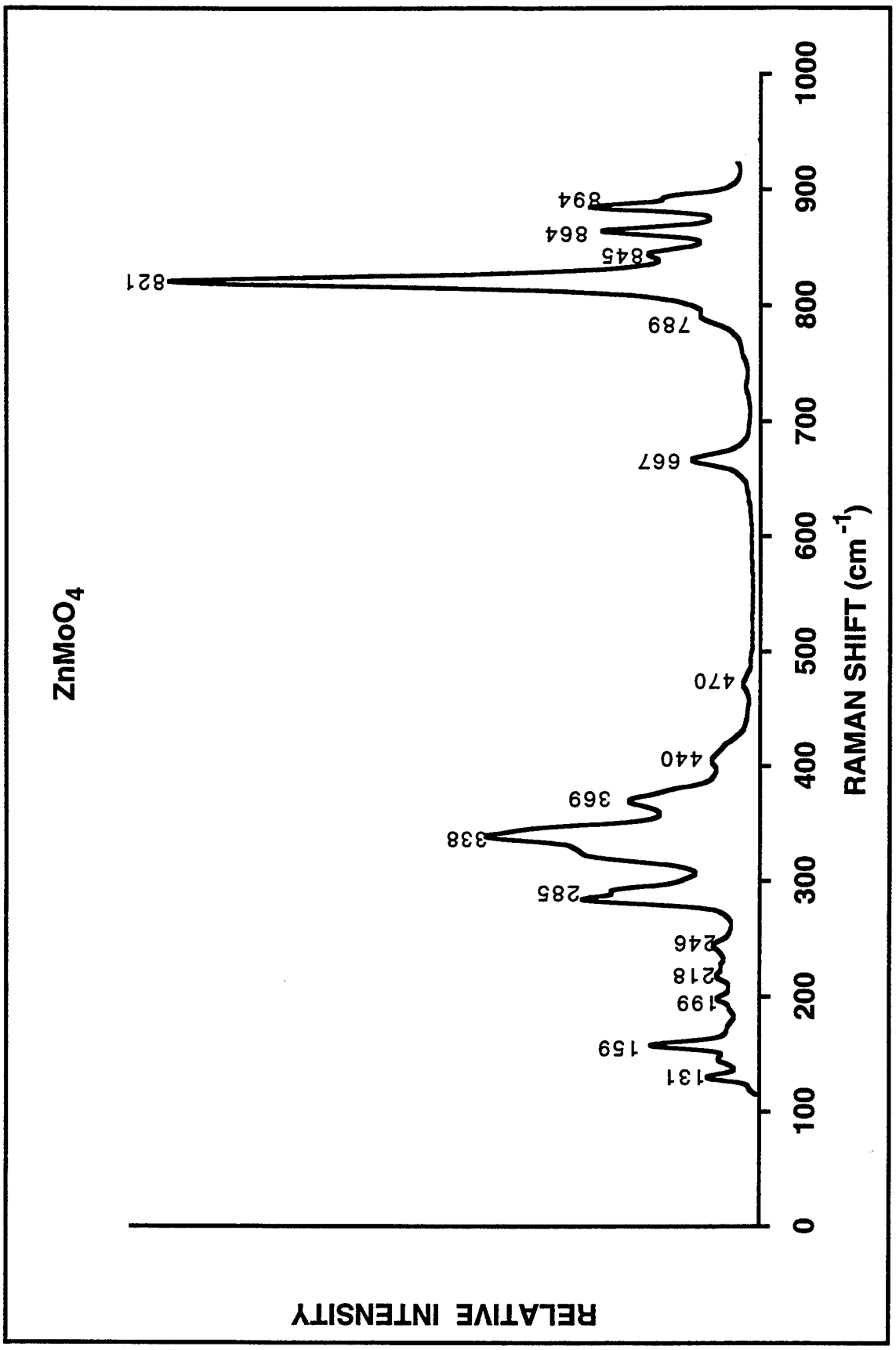

Figure A47. Raman Spectrum of ZnMoO4.

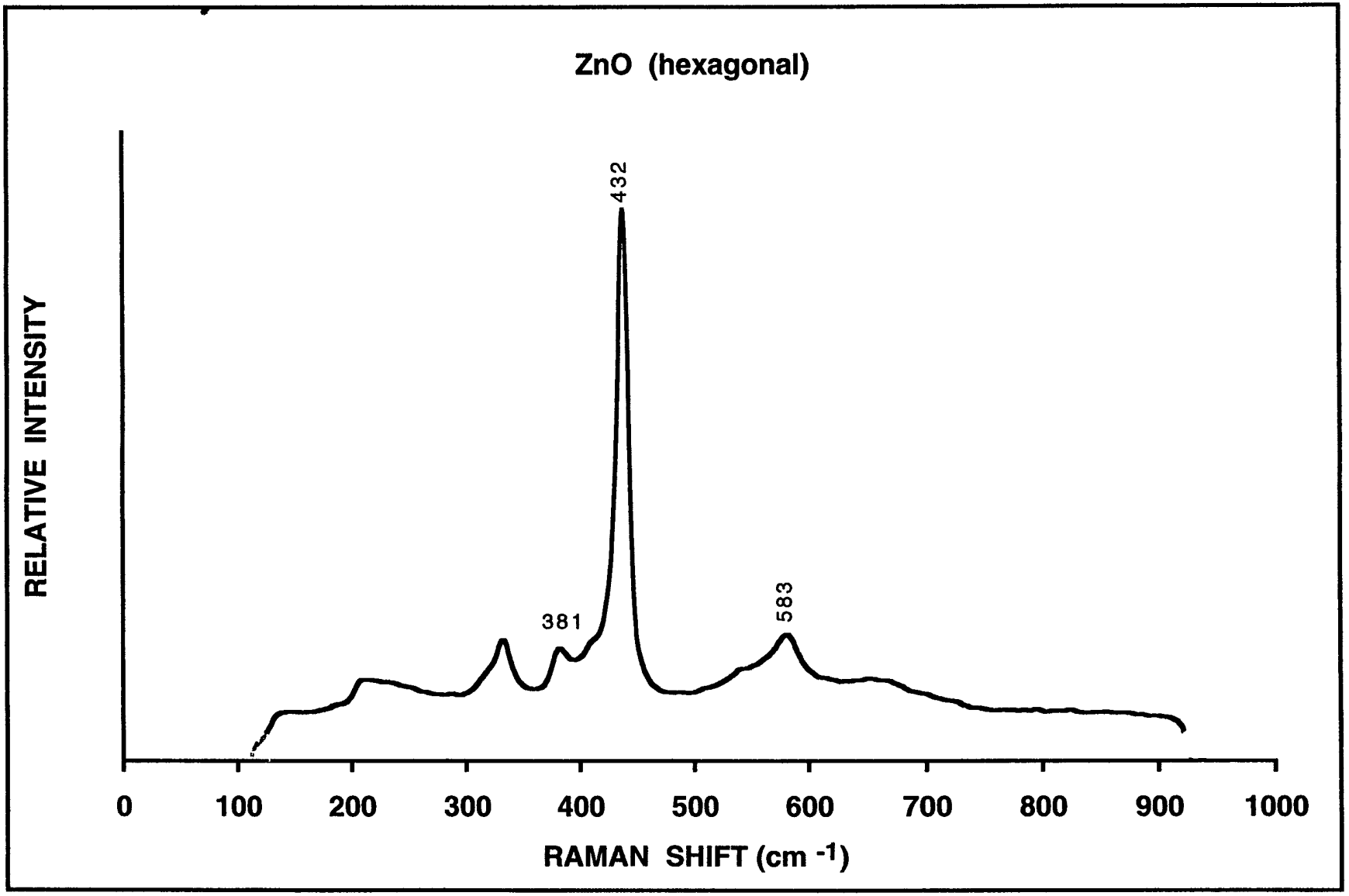

Figure A48. Raman Spectrum of ZnO.

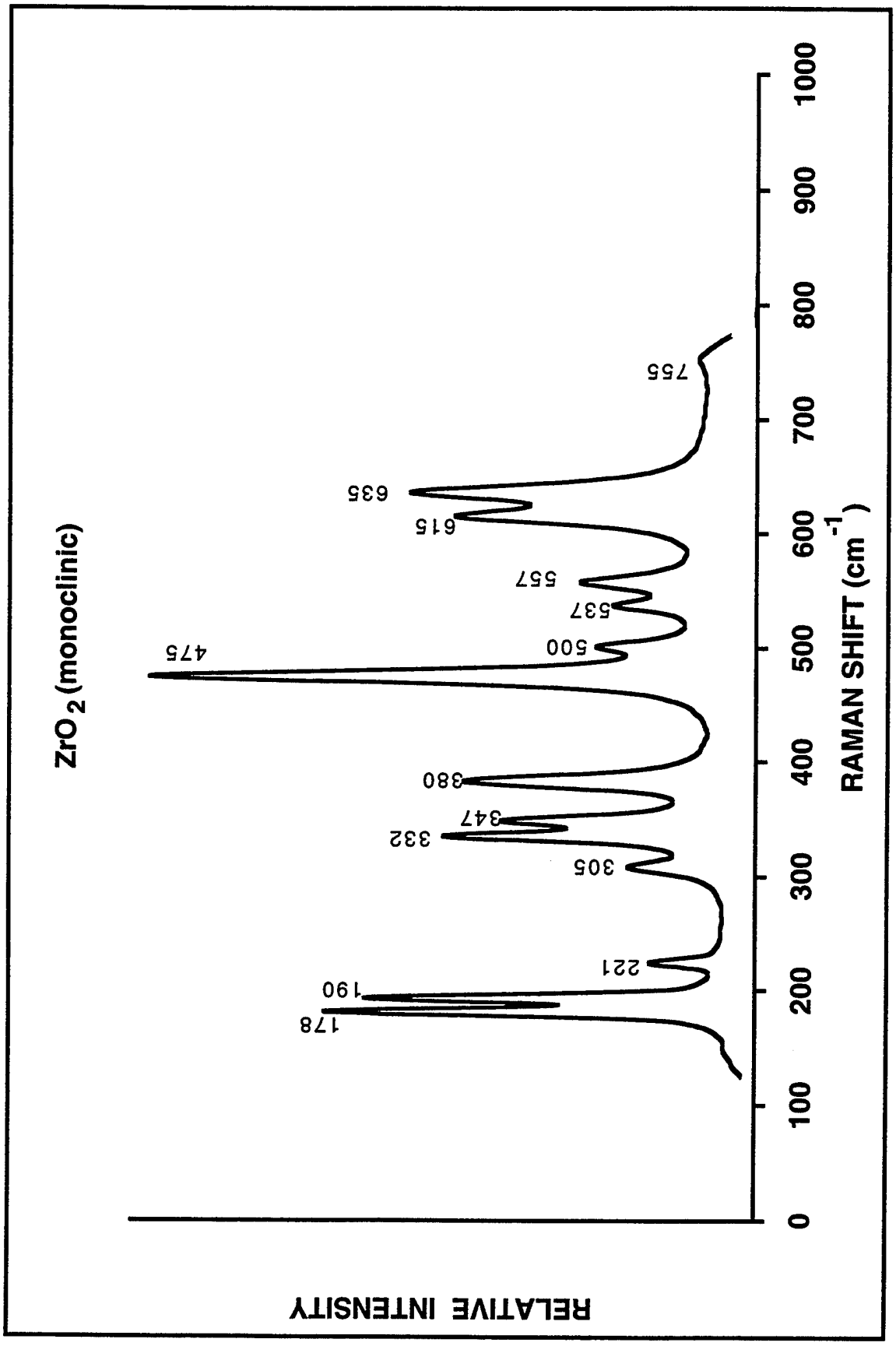

Figure A49. Raman Spectrum of ZrO2.

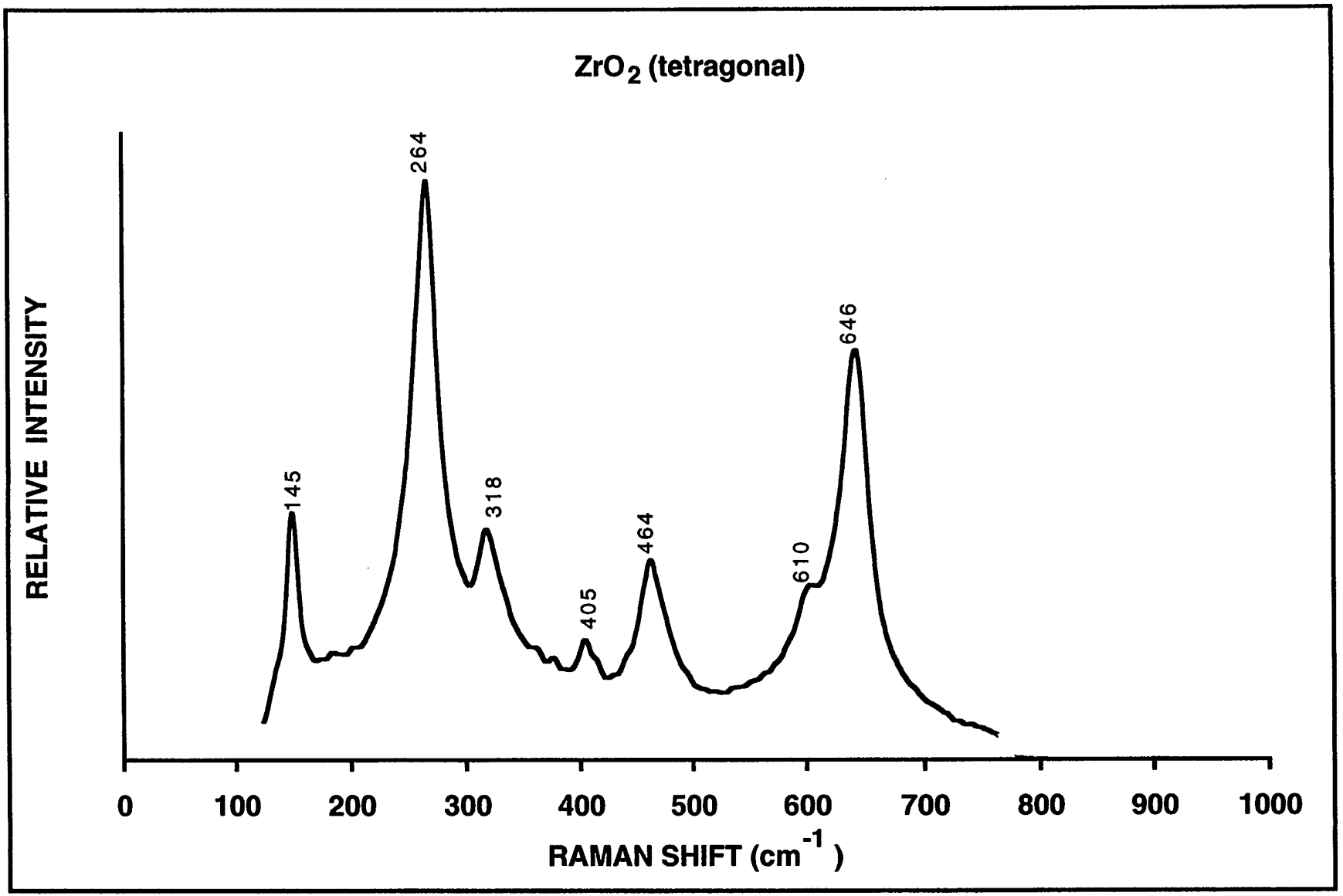

Figure A50. Raman Spectrum of ZrO2.

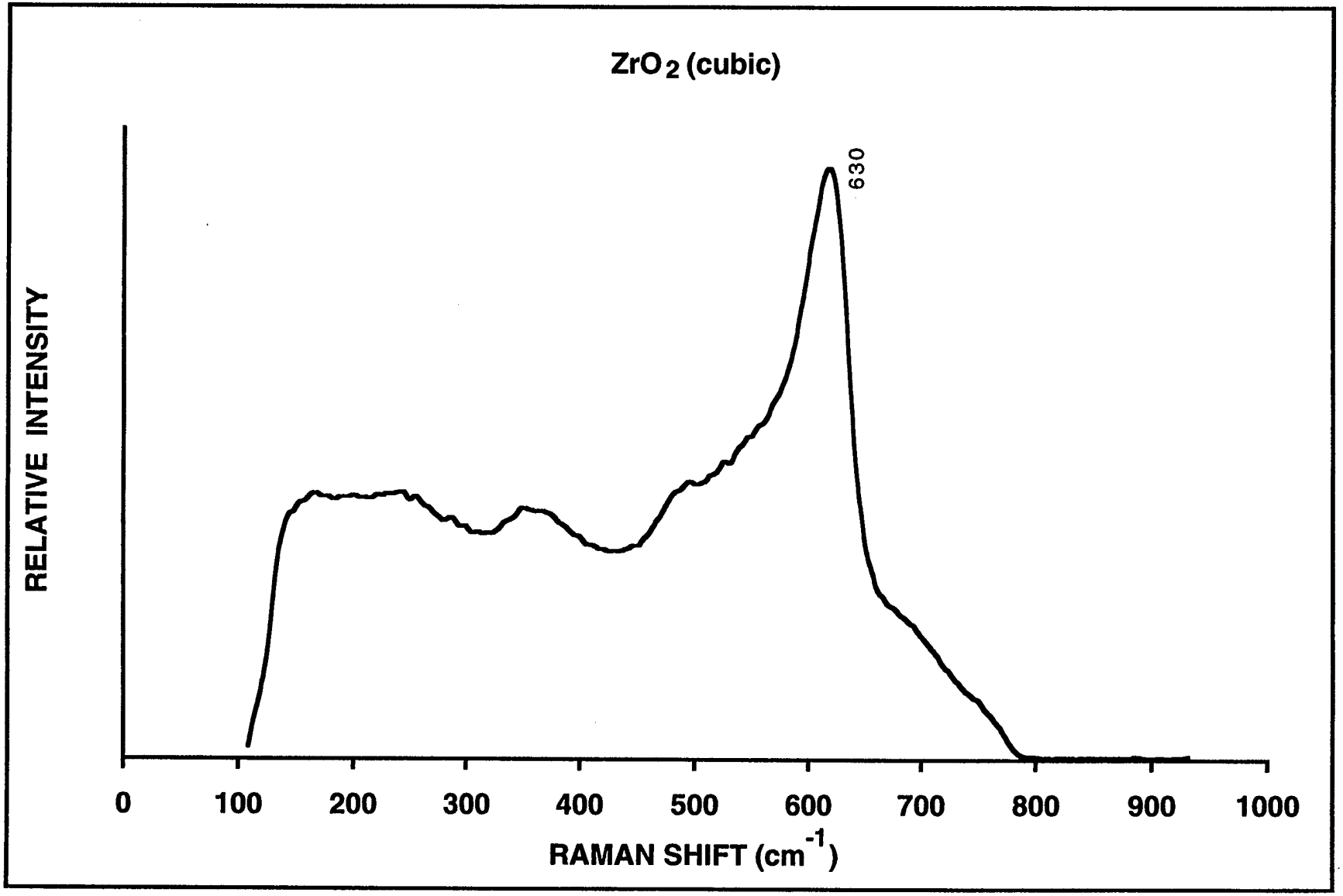

Figure A51. Raman Spectrum of ZrO2.

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